STUDIES IN ADSORPTION

OF

ORGANIC SOLUTES AT INORGANIC SURFACES.

by

C. E. STEWART

A THESIS

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Colour Chemistry Research Laboratory,
Technical Chemistry Department,
The Royal College of Science and Technology,
Glasgow.

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PUBLICATION.

Part of the work in this Thesis concerning adsorption on the anodic oxide film on aluminium has been published in the Journal of the Chemical Society, December 1954, pp. 4360 - 4374.

SUMMARY.

The adsorption of organic compounds from solution by two forms of alumina, the anodic oxide film on aluminium and acidified chromatographic alumina powder, has been studied.

The anodic oxide film used was produced by anodising in chromic acid which yields a highly porous film of almost entirely pure, amorphous or very finely crystalline γ-alumina.

The alumina powder used was acidified by washing with hydrochloric acid.

The adsorption of organic solutes on both substrates from dry organic solvents is found to occur only when the solute molecule contains a hydrogen atom free to form an intermolecular bond. Thus hydroxy- and amino-compounds are adsorbed, presumably by the formation of hydrogen-bonds with the substrate. In the case of the anodic film the adsorption of amino-compounds is prevented by certain solvents whereas adsorption on alumina powder is unaffected by the solvent. This suggests that in the case of the oxide film the N...H...O bond formed in adsorption has lower free energy than the O...H...O bond.

Adsorption involving hydrogen attached to carbon

was also found, e.g. compounds containing acetoxy- and aldehyde groups were adsorbed by the alumina powder. In the case of the oxide film, the results of the experimental work are complicated by suspected decomposition of these solutes.

The part played by the azo-linkage in adsorption on both substrates was examined. Azobenzene is not adsorbed from dry organic solvents on either substrate, but is adsorbed in presence of water.

This seems to be a result of water acting as a hydrogen-bonding cross-linking agent between the solute and the substrate.

In view of the recommendation found in the literature concerning the use of compounds capable of forming lakes with aluminium for colouring anodic oxide films, the adsorption behaviour of two such compounds, viz. alizarin and Solway Blue B, was studied. The irreversible nature of their adsorption suggests that very stable chelate complexes are formed with the aluminium of the oxide film.

The anodic film was found to undergo slight dissolution in aqueous solutions. Owing to the cone-shaped pores of the film, this leads to an increase in the surface area available for adsorption which is a function of the weight of film dissolved. Thus it is important to carry out all adsorption experiments at a constant solution:film weight

ratio, otherwise alterations in the available surface area: film weight ratio, due to dissolution, would lead to inconsistences in the amount of solute adsorbed per unit weight of film.

Both the thermodynamic and kinetic aspects of the adsorption of sulphonated azo dyes by both substrates was studied.

In the case of the oxide film adsorption of these dyes is accompanied by a measureable evolution of heat indicating that a chemical reaction, probably salt formation, takes place between the sulphonate groups and the aluminium. Analysis of isotherm data suggests that the adsorbed anions form a monolayer in which they are oriented in such a way that all their sulphonate groups are attached to the substrate.

There is no measureable heat of adsorption in the case of the acidified alumina powder. The operative mechanism here appears to be one of ion exchange involving the dye anions and chloride ions taken up by the substrate during the pretreatment with hydrochloric acid. The adsorbed dye anions form a monolayer and are oriented in the same manner as those adsorbed on the oxide film.

The affinity of sulphonated azo dyes for both substrates, determined from isotherm data, is the sum of the affinities

of the sulphonate groups in the molecule, each contributing to the total affinity an amount characteristic of its position in the molecule. The aromatic residue or any free hydroxy-groups in the molecule do not appear to contribute to the total affinity.

The apparent heat of adsorption and the apparent entropy of adsorption were determined for several sulphonated azo dyes on the oxide film. Both generally increase with increasing sulphonation of the dye anion. The apparent entropies of adsorption for dyes adsorbed on alumina powder are comparable to those for similar dyes on the oxide film.

The kinetics of the adsorption of sulphonated azo dyes on both substrates were studied. In the case of adsorption on the anodic film the rate of adsorption is controlled, in the earliest stages, by the building up of a layer of dye anions on the outer surfaces of the film followed by diffusion into the pores of the film. Determination of the activation energy of the diffusion process shows that its value is lowest for these dyes most easily removed from solution.

The rate of adsorption of sulphonated azo dyes on alumina powder is controlled, in almost all the cases studied, by diffusion through a liquid film surrounding the particles of alumina. In the earliest stages, however, the rate may

be controlled by diffusion inside the particles of the substrate. The activation energies of adsorption were determined but do not provide further information as to the form of the kinetics.

CONTENTS.

GENERAL INTRODUCTION.

The adsorption of a solute from solution is a complex process depending on the physical and chemical natures of the adsorbent, the solute and the solvent in which the solute is dissolved, and all these various factors must be taken into consideration when an attempt is made to elucidate the mechanism of the process.

One of the most extensively investigated processes of this type is the dyeing of textile fibres and although the substrates studied in the present work are of rather simpler structure, one of them, the anodic film on aluminium, is markedly porous and the adsorption of dyes by it does bear some similarity to the adsorption of dyes by fibres. For this reason a brief discussion of the dyeing of fibres will be given.

Textile fibres are believed to be comprised of both crystalline and amorphous regions, the latter being penetrated by sub-microscopic capillaries or pores. In the dry fibre the dimensions of these pores are too small to allow the passage of dye particles but when the fibre swells on immersion in water the pore-size increases making diffusion of the dye into the fibre possible[1]. This concept of the dyeing process demonstrates the importance of both the diameter of the pores in the substrate and the particle size of the dye in solution. In the case of cellulose, for instance, Haller *et al.*[2] came

to the conclusion that penetration of the substrate by dyes and mordants is dependent on their particle size which must be less than 50 Å, the diameter of the pores being 20 to 100 Å when it is swollen in water at room temperature[3][4]. A great deal of investigation has been carried out on the particle sizes of dyes in solution but so far the results of this work have not contributed much towards a quantitative description of the dyeing process apart from establishing certain generalisations. For example, levelling acid dyes are less aggregated in solution than direct cotton dyes, although the degree of aggregation appears to be characteristic of each dye and decreases with increase in temperature and dilution.

The attraction of the dye molecule to the surface of the substrate is also of great importance. Gee and Harrison[5] suggested that dyeing was the result of the acquisition of an electrical charge by fibres in water whereby they attract or repel dye ions according to the sign of the charge. Neale[6] has elaborated this theory. There are two types of electrical forces involved in the dyeing process, one type is responsible for the formation of covalent or hydrogen-bonds between the dye ions and the fibre, and is effective only over distances of less than 5 Å; the other may be considered as an electrical attraction or repulsion between the dye ion and the fibre and operates at distances up to ca. 100 Å. All textile fibres possess a negative charge in neutral solution which attracts positively

charged colour ions such as those of basic dyes. The colour ions of direct and acid dyes are negatively charged and these should therefore be less readily attracted. This theory is to some extent supported by observations of the neutral dyeing of fibres such as cotton, wool, and silk, but a full discussion is outside the scope of this survey. The energy required to bring the colour ions up to the fibre surface is supplied by the thermal agitation of the solution. A certain fraction of the colour ions which reach the surface is strongly attached to it, by the operation of the short-range forces, forming hydrogen-bonds or some such linkage, depending on the constitutions of the dye and the fibre. Very recently, Derbyshire and Peters[7] have suggested thatpolar forces are of secondary importance in the dyeing of fibres and that the principal contribution to the free energy of dyeing is from non-polar van der Waals forces.

The dyeing process may be considered to involve three stages.

(i) Diffusion of dye through the aqueous solution to the surface of the substrate.

(ii) Adsorption of dye on the outer surface of the substrate.

(iii) Diffusion of dye in the pores of the substrate.

(iii) is generally assumed to be the rate-controlling process. Adsorption takes up a neglible amount of time compared with the diffusion processes and (i) will be much faster than (iii) as the dye molecules are subject to much less mechanical obstruction and the restraining forces are weaker in solution than in the

pores of the substrate.

In the case of a comparatively non-porous substrate, however, such as chromatographic alumina, where the surface available for adsorption is easily accessible, the rate of dyeing may be more dependent on processes (i) and (ii) than (iii).

Diffusion inside textile fibres has been studied by many workers. Neale and his associates have shown that it follows approximately the course predicted by Fick's Law. The rate of diffusion $\frac{ds}{dt}$ of a dye across a unit area at a given point in the substrate is proportional to the concentration gradient $\frac{dc}{dx}$ of the dye at that point, i.e.,

$$\frac{ds}{dt} = - D.\frac{dc}{dx}$$

where D is the diffusion constant.

Neale and Stringfellow[8] applied the equation derived by McBain[9] and tested later by Hill[10] to the dyeing of thin films, where diffusion at the edges may be neglected and the process regarded as one of diffusion into an infinite plane slab of thickness b, i.e.,

$$\frac{C_t}{C_\infty} = 1 - \frac{8}{\pi^2}\left\{ e^{\frac{-\pi^2 Dt}{b^2}} + \frac{1}{9} e^{\frac{-9\pi^2 Dt}{b^2}} + \frac{1}{25} e^{\frac{-25\pi^2 Dt}{b^2}} + \cdots \right\}$$

where C_t and C_∞ are the amounts of dye adsorbed at time t and at equilibrium respectively and D is the diffusion constant. They found that adsorption values calculated by applying this equation agreed quite well with the observed values. A

A further check was obtained by measuring the rate of dyeing different thicknesses of viscose sheets, whereby it was found that the time required to reach a specified degree of saturation is proportional to the square of the thickness of the sheet. The experimental evidence confirmed this relation. Garvie and Neale[11] have shown, however, that the diffusion coefficient calculated according to Fick's Law varies with the concentration of dye and they suggest that the experimental data are better represented by the equation,

$$\frac{ds}{dt} = - D'.C.^{\frac{1}{2}} \qquad \frac{dc}{dx}$$

where D' = a new constant, and C = the concentration of the dye. This is probably because the apparent diffusion coefficient of a dye, which depends on the partition coefficient, varies with the distance into the pores from the outer surface of the fibre. Standing[12] has suggested that the coefficient calculated from Fick's equation, may be regarded as an approximate average value of the diffusion coefficient over the concentration range involved in the experiment.

The rate of dyeing, i.e. the rate of removal of dye from the dyebath, is found to increase with increase in temperature in all cases[13]. The effect of temperature on dyeing rate may be expressed quantitatively by evaluation of the activation energy of the process. Considering diffusion inside the substrate, the theory of activated diffusion developed by

Glasstone, Laidler and Eyring[14] may be applied. This theory explains the high temperature coefficients of diffusion through solids by supposing that the solute molecules must acquire activation energy, E, to overcome the restraint of their surroundings, before they can diffuse. On this basis, Fick's Law applies only to activated molecules whose concentration is proportional to $C.e^{-E/RT}$, (where C = the total solute concentration), and Fick's equation can be applied to the observed concentration gradient if the exponential term is included in the diffusion coefficient, i.e.

$$D_T = D.e^{(-E/RT)}$$

where D_T = the observed diffusion coefficient and temperature T, and D = a constant.

Hence the plot of the logarithms of the diffusion coefficients observed at different temperatures against the reciprocal of the absolute temparature should give a straight line of gradient $\frac{E}{R}$. Garvie, Griffiths and Neale[15] calculated the activation energy for the diffusion of Heliotrope 2B into "Cellophane" sheets by this method and found it to be -14 kcal./mole.

The same treatment may be applied to the overall rate of dyeing to give "activation energies of dyeing". Vickerstaff[13] suggests that these values probably refer to diffusion inside the substrate. The relative importance of diffusion in solution and the fact that the affinity of the dye for the substrate decreases

as the temperature increases, thus decreasing the concentration gradient of the adsorbed dye, may produce an additional effect on rate and render these values less fundamental than those calculated from diffusion data.

The affinity of a dye for a substrate is of fundamental importance. In any reacting system, the equilibrium conditions are governed by the free energy change accompanying the reaction. The free energy change is a measure of the driving force of the reaction and determination of its magnitude for the adsorption process provides a measure of the tendency of the solute molecules to pass from solution on to the adsorbent surface, i.e. the "affinity" of the solute for the adsorbent. Peters and Vickerstaff[16] defined the affinity of a dye for a fibre as the difference between the standard chemical potential of the dye in the two phases, which may be calculated for any system from the following equation:

$$-\Delta\mu^{\circ} = RT \ln.a_1 - RT \ln.a_2$$

where a_1 and a_2 are the activities of the dye in the two phases. Hence the affinity of a dye for any substrate can be determined provided the activity of the dye both in solution and when adsorbed, can be expressed satisfactorily.

In the case of dilute solutions of unionised solutes the activity in solution may be replaced by the concentration as a first approximation. Most dyes, however, are salts of sulphonic

or carboxylic acids and may be regarded as strong electrolytes, i.e., they are completely dissociated into ions in solution, in which case the activity of the dye may be expressed as the product of the activities of the ions.

The fact that solutions of electrolytes do not behave ideally has been accounted for quantitatively, at least for dilute solutions, by Debye and Hückel, on the basis of electrical interaction between ions in solution. It is doubtful, however, whether Debye and Hückel's equation for the activity coefficient, which is applicable to solutions of low total ionic strength containing spherical ions, can be applied to dye solutions, where the ions are not only simple spheres, and in many cases have two or more charges located at specific points in the molecule. Hence, lacking further information, the activity coefficients of the ions must be equated to unity.

The activity of a dye adsorbed on a substrate depends on the manner in which it is adsorbed. For this reason the affinity of a dye for a substrate can only be evaluated when the mechanism of adsorption is known. Three types of adsorption mechanism may be considered. These are:-

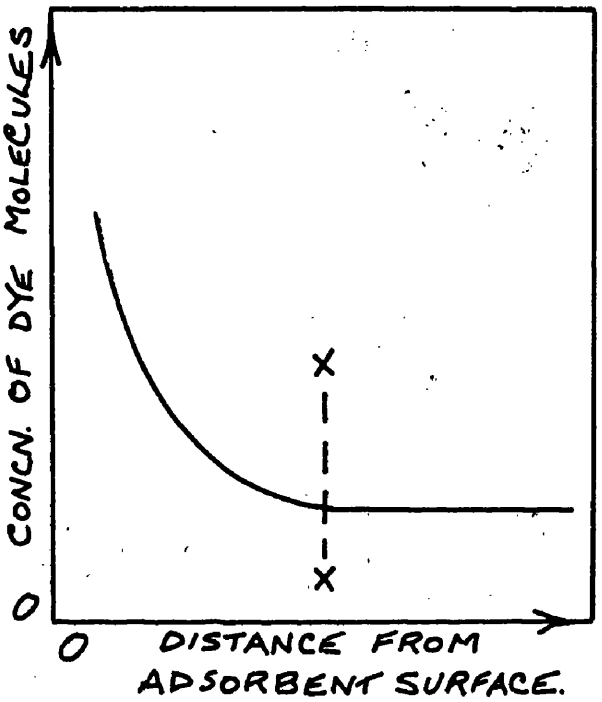
(i) Solute dissolved in the substrate.

(ii) Diffuse adsorption of the solute with possible multimolecular layer formation.

(iii) Solute adsorbed on specific sites in the substrate to form a monolayer.

The adsorption of dyes by cellulose acetate was attributed to mechanism (i) by Kartaschoff[17]. In this case the molar concentration of the solute in the substrate is usually taken as expressing the activity. This is not entirely satisfactory as the volume of the solid phase available for the formation of a dye solution may be considerably less than its total volume.

When adsorption is the result of the existence of an attraction between the adsorbent and the solute which is a function of the distance of the solute molecules from the surface of the adsorbent, adsorption of type (ii) results. Such an attractive force tends to form a layer of solute on the surface, which is opposed by thermal agitation and results in the distribution of solute molecules in solution shown below.



If it is assumed that the volume of solution enclosed between the real surface of the adsorbent and an imaginary surface (XX in Fig.), at which the solute concentration is approximately equal to that in the bulk of the solution, is a separate surface layer in equilibrium with the external solution phase, then the activity of the solute in it is $\frac{S}{V}$, where V = the volume of the phase, and S = the concentration of the solute there, in moles per kilogram of adsorbent.

Type (iii) adsorption may occur when the adsorbent contains a number of reactive sites which attract solute molecules and when occupied are no longer available for adsorption. Gilbert and Rideal[18] have suggested that the dyeing of wool is a process of this type and Lemin and Vickerstaff[19] have based upon it their derivation of an expression for the change in chemical potential of a dye during adsorption on wool.

If it is assumed that the sites are sufficiently far apart for adsorption of a molecule on any site not to interfere with adsorption on adjacent sites, the activity of the adsorbed solute is given by $\frac{\theta}{1-\theta}$, where θ = the fraction of the total number of sites occupied[20]. As in most cases the number of sites is small and they are well spaced out, the assumption is permissible.

In the case of an ionised solute when both ions are adsorbed, the activity is represented by the product of the activities of the ions, e.g., for a dye Na_zD, the activity when adsorbed is

given by:

$$a_{Na_zD} = \frac{\theta_D}{1-\theta_D} \cdot \frac{\theta_{Na}}{1-\theta_{Na}}$$

where θ_{Na} and θ_D refer to the fraction of sites, available for the asorption of Na^+ and D^- ions respectively, which are occupied.

Adsorption is an exothermic process, and is therefore always accompanied by the evolution of heat. The heat change is however usually small and its evalution by direct calorimetric measurement is therefore difficult. Derbyshire[21] has determined calorimetrically the heat of adsorption of the sulphonated azo dye, Naphthalene Orange G (C.I.151) from aqueous solution on to wool, and finds it to be - 9.27 kcal./mole, but when this method is not practicable, the heat of adsorption may be evaluated approximately by applying the Clausius-Clapeyron equation:

$$\Delta H^o = R \frac{T_1 T_2}{T_1 - T_2} \cdot \ln \frac{[S]_2}{[S]_1}$$

where $[S]_1$ and $[S]_2$ are the concentrations of the solute in solution at temperatures T_1 and T_2 respectively which are in equilibrium with one and the same amount of adsorbed solute.

This equation can be applied without knowledge of the adsorption mechanism and, if the temperature range is narrow, the value of the heat of adsorption calculated can be regarded as constant to a first approximation. The values obtained cannot, however, be considered as applying solely to the reaction between

the solute and the adsorbent, because they are the algebraic sum of the heat changes resulting from two successive processes, (i) the removal of solute from association with solvent, and (ii), the attachment of the solute to the adsorbent[7]. They can, however, be used for comparative purposes where the adsorption systems differ in only one component, e.g., in comparisons of the adsorption of a solute from the same solvent, on two different adsorbents. In this instance, some indication is given on the relative strength of the solute-adsorbent bonds in the two cases.

The entropy change accompanying the adsorption process may be evaluated from a knowledge of the heat change and the change in chemical potential involved, by the following equation:

$$\Delta\mu = H - T\Delta S$$

The significance of the entropy change in these processes is still open to discussion. Boltzmann's well-known treatment shows that the entropy of a system is proportional to the logarithm of its probability. In the case of an adsorption system where the solute molecules are rigidly attached to specific sites in the adsorbent, it might therefore be expected that adsorption will be accompanied by a large, negative entropy change, because the solute-adsorbent phase should be much more ordered than the solute-solvent phase. Evaluation of the entropy change may thus be useful in comparing two systems containing the same adsorbent but different solutes. In such a case it may be concluded that the molecules of the

solute whose adsorption involves the greater change in entropy will be more rigidly attached, or more precisely oriented on the adsorbent[13].

PART I.

ADSORPTION ON ANODISED ALUMINIUM

INTRODUCTION .

Aluminium owes its great importance as a raw material in some part to its low specific gravity but mainly to its high affinity for oxygen. It readily reacts with the oxygen in air to form a hard, compact oxide skin which protects the metal from further attack. Anodic oxidation, or anodising, is an electrolytic process for producing thicker and more robust oxide films on the metal than those arising from exposure to the atmosphere. Heavy oxide coatings may be desirable for various reasons, e.g., to increase the naturally high corrosion resistance of the metal, to provide an insulating coating for an electrical conductor, to serve as a key for painting, or for decorative purposes.

The anodising process consists basically in passing an electric current through a suitable acid electrolyte using an aluminium anode and a lead, carbon, or stainless steel cathode. The oxygen liberated at the anode conbines with the anode metal and forms an oxide coating on it. The thickness and properties of the oxide film formed are determined to a great extent by the particular anodising process employed. The type of current, the current density, the nature, concentration, and temperature of the electrolyte, and the time of treatment, are all of great importance. The composition of the anode metal also affects the type of film produced.

The phenomena associated with anodising were first observed by Buff[22] in 1857 but until the first quarter of the present

century the possible use of the electrolytically reinforced oxide film as a means of protecting the metal from corrosion had attracted little attention. In 1923 Bengough and Stuart[23] patented the first process for the protection of aluminium and its alloys in this manner, employing a solution of chromic acid as electrolyte. At the same time they[24] patented a process for coloration of the film by immersion in aqueous solutions of organic dyestuffs. Since 1923 many processes concerned with the production of anodic oxide films on aluminium have been devised and patented, each yielding a film suitable for a particular purpose, but three processes account for most of the anodised aluminium produced commercially at the present day.

The most widely used process is the sulphuric acid process first patented by Gower and Stafford O'Brien and Partners Ltd.,[25] in 1927. The low operating temperature and low, constant voltage employed give this process a distinct advantage over the original Bengough and Stuart process described below. The electrolyte commonly employed is a solution containing 18 to 22% by volume of sulphuric acid. Anodising at 25° with a direct current of 10 to 15 volts for a period of 30 minutes, produces transparent oxide films of about 0.010 mm. average thickness on pure aluminium. The film is ideal for dyeing, the production of true, clear shades of good fastness being relatively easy.

The Bengough and Stuart process, in spite of the necessity for "batch" processing which the voltage control introduces is still widely used. The electrolyte used is a 3% solution of chromic anhydride in distilled or soft water. Anode voltage is raised from zero to 40 volts over a period of 15 minutes, kept constant for 35 minutes, then raised to 50 volts over a period of 5 minutes. The treatment is continued for a further 5 minutes at 50 volts, the total immersion time being 60 minutes. The operating temperature is, for general purposes, $40^{\circ} \pm 2^{\circ}$ but closer regulation may be required to ensure exactly reproducible oxide films, e.g., where a film has to be repeated to match the colours of a dyed finish. The films produced average about 0.005 mm. in thickness and are opaque. Clear, bright shades cannot be obtained on dyeing and, owing to limited penetration of dyestuffs, fastness properties of dyed shades are poor. The film is hence not much used for decorative purposes but has excellent corrosion resistance and is widely employed to protect light metal parts exposed to atmospheric and marine influences. Using a pure aluminium anode, this process yields films which are almost entirely γ - Al_2O_3 with only ca.0.1% of impurity as chromium, thus an adaptation of it was employed in the preparation of the oxide films required in the course of the present investigation.

The third main commercial process is the oxalic acid process first patented by Zaidan, Hojin, Rikagaku and Kenkyujo[26] in

1924. Oxide films of 0.020 to 0.030 mm. average thickness are produced on pure aluminium by a 60 minute treatment in 3 to 8% oxalic acid solution at 25° to 30° and under a constant voltage of 50 to 60 volts. Direct current yields light straw coloured films while alternating current treatment results in brass yellow to bronze films on the pure metal. The colour of the film interferes with some dyed shades but fastness properties are good as the comparatively thick films can absorb considerable amounts of dyestuff.

The differing properties of the anodic films produced by the three commercial processes outlined above supports the statement made earlier that the type of film produced is dependent on the method employed to produce it. Knowledge of the structure and composition of the film is essential from the point of view of elucidating the mechanisms involved in sorption of compounds by the film thus it is relevant to review briefly the work done to determine the mode of film formation and its physical and chemical structures.

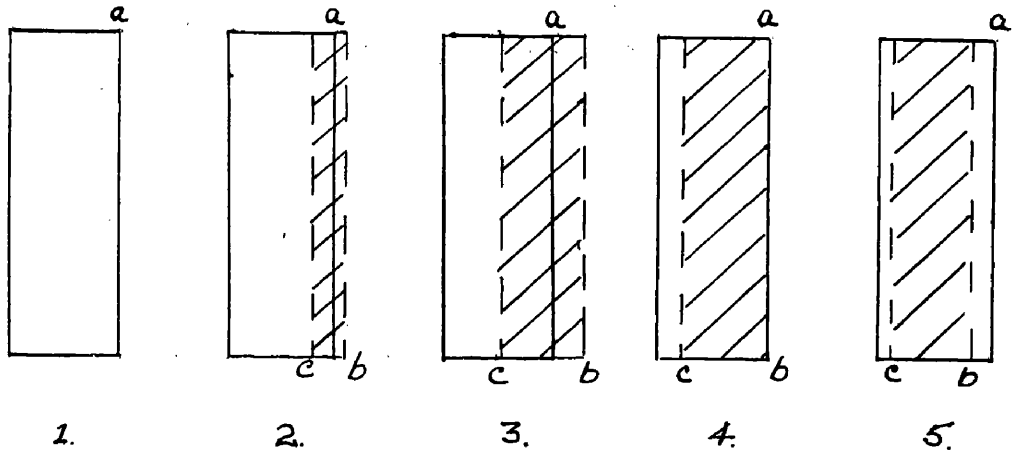
The Formation of the Anodic Oxide Film.

The electrolytes employed in the process of anodising contain no aluminium ions, other than those resulting from unavoidable chemical dissolution of the anode, hence the anodic film can only form at the expense of the basis metal.

Buff[22] discovered that when a current was passed in an

electrolytic cell with an aluminium plate as anode and sulphuric acid as electrolyte, it fell rapidly with time to a very low value but not to zero. Some time later, several investigators[27] found that the flow of current could be maintained if the applied voltage was increased. The required voltage depends on the nature of the electrolyte used, and increases with time to a maximum value characteristic of the electrolyte. It was found that the higher was the voltage characteristic, the thinner was the film formed. Gunther-Schulze[27] concluded that the material forming the anodic film must be of itself non-conducting, but was porous, its effective conductivity being dependent on the total cross-sectional area of the pores. When an electrolyte is employed in which the film is appreciably soluble, as is the case with the electrolytes used commerically, the cross-sectional area of the pores increases especially at the outer surface, and the thickness of the film attains an equilibrium value when the rate formation is equal to the rate of solution of the outer layers. Beyond this point the outer layers are subject to solution more rapidly than the new film is formed, and the film tends to become loose and powdery.

The individual stages of film formation are represented below.



▨ = OXIDE

a = ORIGINAL BOUNDARY OF METAL ; b = OUTER BOUNDARY OF OXIDE ;

c = METAL/OXIDE INTERFACE.

At stage (4), the total change in the thickness of the metal plus oxide is zero. As anodising continues, stage (5) is reached where the film thickness is reduced until the combined thickness of the metal and oxide is less than that of the metal originally. The extent of this action depends largely on the nature of the electrolyte, solution occurring to a greater extent with sulphuric than with chromic acid, stage (4) represents the point at which rate of film formation is balanced by rate of solution.

The actual mode of formation of the films has been intensively studied. Theories that the primary reactions involved is the formation of aluminium hydroxide have been proposed by several workers. Ginsberg[28] suggested that the hydroxide is initially formed by chemical means and is dehydrated and hardened by spark

discharge to form the oxide. This mechanism is unlikely as there is no evidence of sparking occurring during formation. Lilienfeld, Nieh, and Goldman[29] later proposed a theory which also assumed the formation of the hydroxide. They suggested that dehydration resulted from a mechanical pressure arising from the electric field produced in the hydroxide which functions as a dielectric between the anode and the electrolyte. The pressure forces the water from the hydroxide to form a hard, compact layer of oxide. It has not been observed with any degree of certainty, however, that hydration occurs at any stage of the process.

Other conjectures frequently made in the literature that the aluminium salt initially formed at the anode is hydrolysed and precipitated as $Al(OH)_3$ which then migrates electrophoretically to the anode and is there dehydrated are not supported by consideration of the conditions obtaining at the anode. Jenny and Lewis[30] point out that the occurence of hydrolysis is improbable when the reaction of the strongly acid electrolyte is unlikely to attain the neutral point in the neighbourhood of the anode. In any case, the hydroxide formed would be positively charged and would not migrate to the anode.

As a result of investigating films formed in electrolytes having little or no solvent action on them, Gunther-Schulze[31] proposed that the primary reaction was a result of the direct combination of the anode metal and oxygen. He suggested that

the film was made up as follows:

(a) A continuous skin of molecular thickness covering the metal.

(b) A gas layer in the pores of an oxide film.

(c) A solid porous film filled with electrolyte.

(a) is the naturally-occurring film which is pierced by incoming O^{--} ions when the anodising current is passed. The incoming ions transfer their charges to the surface and form an oxide layer which is later pierced by ions arriving later. In this way a porous oxide is formed. Most of the subsequent ions do not reach the metal but give up their charge on meeting an obstacle of high resistance and in so doing free electrons which are alone capable of piercing the layer of high resistance. This occurs at the junction of the electrolyte and gas layer(b) and the solid film(a). A few ions do, of course, penetrate to the metal and form more oxide while those neutralised at the junction of (a) and (b) reinforce the gas layer. Later, Setch and Miyata[32] supported the concept that the film was a result of the direct reaction between the metal and oxygen. The initial layer so formed is sufficiently porous to allow oxygen ions and the anodising current to flow through it, thus the film grows continuously from the initial active layer. In the case of anodising with sulphuric acid as electrolyte, the O^{--} ion, having a discharge potential of + 1.23 volts is discharged preferentially to the SO_4^{--} ion with its higher discharge potential of + 1.9 volts. The oxygen, in the extremely active form in which

the O^{--} ion exists, combines with the similarly highly active aluminium to form Al_2O_3 directly. Since the reaction takes place in aqueous solution, water can take part in the decomposition so that the oxide formed may be hydrated to a greater or lesser extent depending on the conditions obtaining.

The course of the reaction may be formulated as follows:

$$2\ Al + 3\ O = Al_2O_3$$

$$\text{or } 2\ Al + 3\ O + H_2O = Al_2O_3.H_2O \quad \ldots\ldots \text{(i)}$$

the film formed and the aluminium then dissolve in the dibasic acid H_2R in accordance with the equations:

$$3\ H_2R + Al_2O_3 = Al_2R_3 + 3\ H_2O$$

$$\text{or } 3\ H_2R + Al_2O_3.H_2O = Al_2R_3 + 4\ H_2O \quad \ldots \text{(ii)}$$

$$\text{and } 3\ H_2O + 2\ Al = Al_2R_3 + 3\ H_2 \quad \ldots \text{(iii)}$$

Solution occurs predominantly in accordance with (ii), at least in the equilibrium state where a balance is maintained between formation of the film and its dissolution, whilst solution of the metal, which takes place in accordance with (iii) is of subordinate importance under the operating conditions usual in the commercial processes.

Examination of the film formed in sulphuric acid by Akimov, Tomaschov and Tinkina[33] showed a thin, dense layer of slightly hydrated oxide adjacent to the aluminium surface with a thick, porous layer of hydrated oxide on the outside. They agree with the theory that the thin layer is the result of direct combination

of the aluminium and oxygen, and suggest that the porosity of the outer layer is due to the solvent action of the sulphuric acid which produces irregular cone-shaped fissures.

A theory proposed by Mott[34] to explain the formation of oxide films on aluminium and similar metals in air provides a reason for their limiting thickness. The theory may basically apply to electrolytical formation of films. He suggested that formation is a result of the diffusion of metal ions and electrons through the oxide layer. If the electrons have sufficient energy to diffuse to the outer surface of the oxide layer, combination will occur between metal ions and oxygen at the surface to form new layers of oxide. Electrons can penetrate an insulating layer up to a distance of about 50Å without receiving any energy of excitation. This theory, known as the quantum mechanical tunnel effect, is the basis of Mott's theory. He[35] later proposed another theory in which he assumed that oxygen ions are adsorbed on the surface, setting up a strong electric field, in the course of electrolytic oxidation. The metal ions can migrate under these strong electric fields although their solubility in the oxide at the temperatures considered is very small to allow their passage. By both treatments he arrived at the value of work function required for diffusion of the metal ions and electrons, which are comparable, and lead to the limiting value of film thickness usually found. He states, however, that insufficient experimental data is available

to determine which theory is correct.

A very comprehensive theory which accounts for most of the general characteristics of the film has been proposed by Anderson[36]. He has shown that the compact, barrier layer of oxide separating the metal from the porous oxide layer is the seat of growth processes from which the porous film originates. The barrier layer is formed by diffusion of Al^{+++} ions of radius 0.5Å, under the influence of an intense electric field, ca. 10^7 volts/cm., to the solution. Electrical conductance within the film allows O^{--} ions, with a comparatively large radius of 1.3Å, to pass through the film when sufficient space has been created by the diffusion of Al^{+++} ions. For every three Al^{+++} ions involved, two combine with O^{--} ions to form oxide and one diffuses into the solution where it forms a soluble salt with the acid. This theory accounts for the porosity of the film and for its excellent adherence to the metal, as the oxide film grows outwards with the barrier layer always in good contact with the aluminium. Such a mechanism is also considered necessary to account for the spatial arrangement of the aluminium and oxygen atoms in the film.

Structure and Composition of the Oxide Film.

When electrolytes having little or no solvent action on the film are used for its production, it remains extremely thin, ca. 1μ, and fine pored. Appreciably solvent electrolytes, such as sulphuric, chromic and oxalic acids yield thick films as they ensure

the maintenance of adequate pore cross-section which allows the passage of the relatively large leakage current required for growth.

Akimov, Tomaschov, and Tinkina[33] found evidence of irregular cone-shaped fissures in films formed in sulphuric acid. Edwards and Keller[37] obtained electron micrographs which suggested a porous structure in which the pores widened as they approached the outer surface of the film. Rummel[38] photographed the cross-section of an oxidised aluminium sheet perpendicular to the surface. The photographs obtained show that the pores run comparatively uniformly at right angles to the metal surface. Assuming the cross-section of the pores to be circular, he calculated their diameter to be about 0.1μ. Evidence obtained by a study of the permeability of films produced by complete anodising of aluminium in chromic and sulphuric acids, led Burwell and May[39] to suggest that the film is not entirely penetrated by pores, but that an impervious barrier layer exists. X-ray examination of films, without stripping them from the metal, after they had been dyed with Alizarin S was carried out by Bradshaw and Clarke[40]. The dye was found to have penetrated about half way through the film over most of its surface but in places penetration had occurred through the entire thickness of the film.

Many workers who have studied the film by X-ray and electron diffraction methods state that the oxide has an amorphous structure,

while others maintain that it is crystalline. X-ray diffraction patterns for films formed in oxalic acid were obtained by Schmid and Wassermann[41] which showed two broad diffuse rings ascribed by them to the anhydrous oxide γ- Al_2O_3. Burgers, Claassen and Zernike[42] obtained sharp γ- oxide patterns for films produced in boric acid, but this is not conclusive since the electrolyte was used at boiling point. Broad diffuse γ- oxide bands for the films as formed and sharp patterns for films subsequently boiled in water were obtained by Harrington and Nelson[43] for films produced in sulphuric, oxalic and phosphoric acids. From the width of the diffuse bands they calculated that the grain size of the material as formed, if crystalline, was 12Å, less than twice the edge of the unit cell of γ- Al_2O_3 (7.90Å). As they point out, there is little real difference between an amorphous material and a crystalline material of this grain size. They readily identified the patterns of the boiled film as those of the monohydrate, bohmite. Other workers[44] state that the film as formed is amorphous and on heating is converted to cubic γ- Al_2O_3. Pullen[45] states that the film appears to be amorphous, as far as X-ray and electron diffraction methods can determine, but suggests that this observation is probably due to the crystals being too small to give a pattern.

Evidence that the crystalline form of the film is independent of the electrolyte used was put forward by Taylor, Tucker and

Edwards[46]. They obtained γ - oxide patterns for films formed at applied voltages of over 100 volts in various electrolytes.

Chemical analyses have been made by numerous investigators and lead to the conclusion that the film consists of aluminium oxide with quantities of adsorbed water and some occluded electrolyte.

For films formed in chromic acid, various authors[45][47] have published figures which are consistent and show that the film is practically anhydrous with only a trace, ca.0.1% of chromium.

The figures published for films formed in oxalic and sulphuric acids are somewhat divergent. Baumann[48] states that films formed in oxalic acid approximate to $2\ Al_2O_3.H_2O$ while Pullen[45] gives $Al_2O_3.H_2O$. Films formed in sulphuric acid contain about 13% of the electrolyte as basic sulphates.

Factors affecting the Formation and Structure of the Oxide Film.

The effect of the nature of the electrolyte on the formation and structure of the oxide film has already been mentioned. In any one process using a particular electrolyte there are, however, several other variables which have an effect on the type of film formed.

(1) The operating temperature of the process.

As the solvent action of the electrolyte is increased by increase of temperature, film thickness varies with the operating

temperature of the anodising process. The pores of the film taper towards the interior and high temperature increases the taper of the pores by resulting in increasing dissolution of the outer layers of the film. This explains the fact that adsorption of dyes by the film increases with the temperature at which they are formed[49].

(2) The current density.

Tarr, Darrin and Tubbs[50] found that the amount of aluminium oxidised is directly proportional to the current density. Current density increases as temperature increases hence high temperatures should result in thicker oxide coatings. In practice, as solution of the film in the electrolyte is greater at higher temperatures, the effect of high current densities is probably cancelled out.

(3) Time of treatment.

Although the thickness of the film formed is a function of the time of treatment, the limiting factor in film thickness is the solvent action of the electrolyte. As anodising continues the anode decreases in thickness until ultimately it becomes so thin that it melts due to the great resistance. The passage of current is interrupted at this point so that very small pieces of the metal are always formed in the interior of the film.

(4) The composition of the basis metal.

The current density on a surface being anodised as well as being affected by the nature and temperature of the electrolyte,

is varied by the alloying elements in the anode metal. Possible variations in current density from one part of the surface to another are important since these cause variations in the thickness and appearance of the anodic film. Ellsner[51] found that under similar anodising conditions, much thicker films are produced on pure aluminium and aluminium-magnesium-silicon alloys than on aluminium-silicon or duralumin type alloys. The difference between the effects due to alloying elements in solid solution and those which are present as unadsorbed components is indicated by several workers[52], who found that free silicon and $MnAl_6$ are not dissolved or oxidised to any extent but remain dispersed in the anodic film, which they darken. All other constituents dissolve in the commercial electrolytes, but some only do so rapidly as long as they maintain contact with aluminium. If contact is broken they remain undissolved as an impurity in the film. Irregular film thickness may result where an alloying element is entirely in solid solution as current flow, and hence anodising, may occur preferentially in the neighbourhood of the grain boundaries.

The colour of the anodic film is also modified by the presence of alloying elements. Films produced on silicon or manganese containing alloys in sulphuric acid are grey, as are films produced on silicon containing alloys by the oxalic acid process.

Dyeing of the Oxide Film.

Since Bengough and Stuart[24] took out the first patent for

colouring anodised aluminium by the application of water soluble dyes a considerable amount of work on the subject has been reported, mainly in the patent literature. Most of this work has, however, been of an empirical and practical nature and the mechanism of the dyeing process has not been investigated quantitatively.

The dyeing of the anodic film has been compared with the adsorption of dyes on alumina powder by Haller[53] who found that both the film and the powder were dyed uniformly to the same shade by acid dyes, while basic dyes did not dye the film at all. When alumina powder was shaken with solutions of basic dyes and then allowed to settle, it was found that the heavier particles settled down undyed while the finer particles were dyed. He suggests that the relative sizes of the oxide grains and the dye particles may thus be of importance.

The types of dyes which are suitable for colouring the film have been described by Henley[54] who has also discussed the factors on which the choice of dye should be based. Gill[55] has made an extensive survey of the methods of dyeing the film and of the dyes with regard to their level-dyeing properties and their fastness to light, heat and water. He states that the best dyed results appear to be obtained with dyes which are capable of forming co-ordinated complexes or lakes with the alumina of the film. Very recently, Speiser[56] has suggested that lake-forming

dyes colour the film by forming a chemical complex with the oxide, whereas the fixation of acid and direct dyes is due to physical forces. He also states that basic dyes do not colour the film unless it is pre-treated with certain collagen substances, and suggests that these substances form a chemical complex with the dye. No quantitative work has, however, been reported or conclusive evidence produced to prove the operation of these mechanisms.

EXPERIMENTAL.

Preparation of the Oxide Film.

(a) Anodising equipment.

The anodising cell was a 2 litre beaker immersed in a thermostat so that rigid temperature control could be maintained throughout the anodising process. The cathode was a lead plate (6 x $3\frac{1}{2}$ x $\frac{1}{8}$ in.) and the anode a strip of aluminium foil of the same area. A perspex frame held the electrodes at a fixed distance apart. Any slight variations in temperature over the anode surface were eliminated by the provision of an electrically driven stirrer, operating at slow speed, which kept the electrolyte constantly agitated. Uniform thickness of the oxide film over the anode surface was thus ensured. The cell (Fig.1) was connected in the anodising circuit (Fig.2) with a voltmeter across the electrodes, an ammeter in series with the main circuit and a variable resistance to adjust the output from the rectifier.

The electrolyte used was a 3% solution of "Analar" chromium trioxide in distilled water. The electrolyte was chosen because of the high purity of the films formed in it.

The basis metal was aluminium foil in a high state of purity (99.99%) since the presence of impurities in the anode has been shown to have a considerable effect on the constitution of the film (see p.28). The foil was obtained through the courtesy of The British Aluminium Co. Ltd.

(b) Anodising procedure.

The foil was cut to a size corresponding to that of the lead anode and lightly marked into strips ($3\frac{1}{2}$ x $\frac{1}{4}$ in.). It was thoroughly degreased by wiping over with a cotton wool pad soaked in carbon tetrachloride, wrinkles being smoothed out at the same time so as to present a flat surface for anodising. After further washing with water the foil was inserted as anode in the cell. Anodising was carried out for 2 hours at 45° using rectified alternating current and an applied voltage of 45 volts. This ensured a current density of ca. 6 amps/sq.ft. On completion of anodising the anode was removed from the cell and washed with water to remove any adhering electrolyte. The anodised foil was dried by pressing between two filter papers to remove loose water followed by oven drying at 130° for one hour. Prior to use in sorption experiments the foil was kept in a dessicator, but never for more than twenty four hours after anodising as the absorptive capacity of the film deteriorates if a longer period is allowed to elapse.

The procedure described above was strictly adhered to, as slight variations in anodising conditions may affect the properties of the film formed considerably and it was essential for exactly similar films to be used throughout the experimental work. Care was taken not to handle freshly anodised films as grease is readily absorbed and effectively seals the pores of those parts of the film

which come in contact with the skin.

Estimation of the Oxide Film.

The method suggested by Edwards[57] was used to determine the weight of oxide on the strips ($3\frac{1}{2}$ x $\frac{1}{4}$ in.) cut from the anode. Each strip was immersed in 50 ml. of a boiling solution containing phosphoric acid (85%: 35 ml.) and chromium trioxide (20g.) per litre of distilled water. By weighing the strip before immersion and after immersion and drying the amount of oxide present was given by the difference in the two weights. In practice, a 5 minute treatment was found sufficient. The average weight of oxide on strip of 0.875 sq.ins. area was estimated as ca.0.15g.

Dyes and other Reagents Used.

The adsorption characteristics of the following compounds on the anodic film was studied.

Azo-compound.

Azobenzene

A pure sample of this compound was prepared by recrystallisation of a commercial sample and checking the purity by melting-point determination.

Hdyroxy-compounds.

(i) 2:4-Dinitrophenol

(ii) 2:4-Dihydroxyazobenzene

A pure sample of (i) was obtained by recrystallising a laboratory sample and checking its purity by melting-point determination

Compound (ii) was prepared by diazotising aniline and coupling with resorcinol. It was purified by recrystallisation and its purity checked by melting-point determination.

Amino-compounds.

(i) Phenylazo - 1 - naphthylamine

(ii) Phenylazo - 2 - naphthylamine

(iii) Magenta P (C.I.677)

(i) and (ii) were prepared in the normal manner from aniline and 1- and 2- naphthylamine respectively, and purified by recrystallisation.

(iii) was prepared by recrystallisation of a commercial sample.

Acetoxy-compounds.

(i) Glycerol triacetate

(ii) 2:4-Diacetoxyazobenzene

Pure glycerol triacetate was prepared by redistillation of a commercial sample. Compound (ii) was prepared by acetylation of the dihydroxy-compound in the normal manner.

Methoxy-compounds.

(i) 2-Methoxynaphthalene

(ii) Dimethylterephthalate

(iii) 2:4-Dinitroanisole

Pure laboratory samples used.

Lake-forming compounds.

(i) Alizarin

(ii) Solway Blue B (C.I. 1054).

Compound (i) was prepared from a commerical sample of sublimation and its purity checked by melting-point determination.

(ii) was prepared by recrystallisation of a commercial sample.

Sulphonated azo-compounds.

Sodium salts of the compounds listed below were used in every case and are referred to subsequently by the names given in parenthesis.

		Colour Index No.
(i)	Sulphanilic acid ⟶ 1-naphthol (Orange I)	150
(ii)	o-Methyl derivative of (i) (Methylated Orange I)	
(iii)	Sulphanilic acid ⟶ 2-naphthol (Orange II)	151
(iv)	1-Naphthylamine-4-sulphonic acid ⟶ 2-naphthol (Naphthalene Red J)	176
(v)	Aniline ⟶ 2-naphthol-3:6-disulphonic acid (Aniline ⟶ R-acid)	38
(vi)	1-Naphthylamine ⟶ 2-naphthol-3:6-disulphonic acid (1-Naphthylamine ⟶ R-acid)	88
(vii)	p-n-Butylaniline ⟶ 2-naphthol-3:6-disulphonic acid (Butylaniline ⟶ R-acid)	

		Colour Index No.
(viii)	p-n-Dodecylaniline ⟶ 2-naphthol-3:6-disulphonic acid (Dodecylaniline ⟶ R-acid)	
(ix)	Sulphanilic acid ⟶ 2-naphthol-6-sulphonic acid	
(x)	1-Naphthylamine-4-sulphonic acid ⟶ 2-naphthol-6-sulphonic acid (Naphthalene Red EA)	182
(xi)	Aniline ⟶ 1-acetylamino-8-naphthol-3:6-disulphonic acid (Azogeranine)	31
(xii)	p-n-Butylaniline ⟶ 1-acetylamino-8-naphthol-3:6-disulphonic acid (Butylazogeranine)	
(xiii)	p-n-Dodecylaniline ⟶ 1-acetylamino-8-naphthol-3:6-disulphonic acid (Dodecylazogeranine)	
(xiv)	Aniline ⟶ 1-amino-8-naphthol-3:6-disulphonic acid (Aniline ⟶ H-acid)	
(xv)	p-n-Butylaniline ⟶ 1-amino-8-naphthol -3:6-disulphonic acid (Butylaniline ⟶ H -acid)	
(xvi)	Sulphanilic acid ⟶ 2-naphthol-3:6-disulphonic acid (Sulphanilic acid ⟶ R-acid)	
(xvii)	1- Naphthylamine-4-sulphonic acid ⟶ 2-naphthol-6:8-disulphonic acid (Naphthalene Scarlet 4R)	185
(xviii)	Dianisidine ⟶ (1-amino-8-naphthol-2:4-disulphonic acid)$_2$ (Sky Blue FF)	518

Pure samples of compounds (i),(iii),(iv),(vi),(x),(xi),(xiii), (xvii) and (xviii) were prepared from commercial samples by one of two methods. Compounds (iv),(x),(xvii) and (xviii) were purified by passage down a column of anionic and cationic resins in series, the resultant free acids being subsequently neutralised with sodium hydrogen carbonate. The remainder were purified by salting out from aqueous solution with sodium chloride followed by recrystallisation from ethanol-water mixture. Compound (ii) was prepared by methylation of a 100% pure sample of (i).

All other sulphonated azo-compounds were prepared in the laboratory by diazotising the appropriate amine and coupling with the appropriate naphthol. Purification was effected by salting out and recrystallising.

Pure samples of the naphthols required were available except in the case of 1-acetylamino-8-naphthol-3:6-disulphonic acid, used in the preparation of compounds (xii) and (xiii). This was prepared from 1-amino-8-naphthol-3:6-disulphonic acid by the method described by Fierz-David and Blangey[58]. The amino-compound was acetylated in sodium carbonate solution by using acetic anhydride. Complete acetylation of the amino-group occurs and the hydroxy-group is partially acetylated. When

acetylation was complete sodium carbonate was added to the solution which was then heated to 90° to 95° for one hour. This treatment hydrolyses the acetyl group on the oxygen but does not attack the acetyl-amino group. The resulting alkaline solution was used directly in the coupling reaction.

The purity of all the sulphonated azo-compounds was determined by reduction with titanous chloride as described by Knecht(59). All samples used in the experimental work were of over 95% purity as estimated by this method.

Adsorption Procedure.

5 ml. of a solution of the compound under investigation was placed in a soda glass test tube together with a weighed strip ($3\frac{1}{2}$ x $\frac{1}{4}$ in.) of anodised foil. The tube was then completely sealed in a bunsen flame and immersed in a thermostat tank at the required experimental temperature. Constant agitation of the contents of the tube was effected by attaching it to an electrically driven horizontal shaft, revolving at 35 r.p.m., under the water in the thermostat tank.

For measurements of the rate of adsorption several tubes containing 5 ml. portions of a solution of one concentration, usually 0.02% by weight of solute, were placed in a thermostat. These were removed and their contents analysed at various time intervals measured from the time of immerstion. The state of the solution/oxide film system could thus be specified after the

adsorption process had continued for different periods of time. Analyses of contents of tubes removed after a period of immersion, which varied with solute and experimental temperature, from ca. 2 hours to ca. 24 hours, showed constant distribution of the solute between film and solution. This indicates that the system has reached the equilibrium state.

Adsorption isotherms were plotted from results obtained by immersing a number of tubes in the termostat each containing one of a range of concentrations of solute, usually 0.02% to 0.2% by weight. The tubes were allowed to remain in the thermostat until sufficient time had elapsed for equilibrium to be attained.

The amount of solute adsorbed by the oxide was determined by noting the difference between the initial and final concentration of the test solutions.

Slight variations in the size of the anodised pieces, and hence in the amount of oxide, used in each tube were allowed for by stripping and weighing each piece on removal from the tube when the experiment was completed. This weight was substracted from that measured before immersion of the strip in the test solution, the difference representing the weight of oxide.

Analytical Techniques.

(1) Estimation of concentration of solutions of compounds studied.

The concentrations of solutions of the compounds under

investigation were determined by photoelectric absorptiometry with a tungsten or mercury vapour lamp as light source.

Solutions containing dyes and other coloured compounds were measured using a Hilger "Spekker" adsorptiometer with a tungsten lamp.

The concentrations of solutions of colourless solutes were measured using a Unicam S.P. 500 photoelectric spectrophotometer with an ultra-violet light source. Ultra-violet adsorption spectra for the solutes in the solvents employed in the adsorption experiments were first obtained and all subsequent readings taken using light of the wavelength most strongly adsorbed by each solute. In cases where it was suspected that the solute had decomposed as a result of treatment with the anodised foil, comparison of ultra-violet spectra obtained before and after the adsorption experiment usually indicated whether or not decomposition had occurred.

It was found that the pH of neutral solutions which had been in contact with the anodised foil increased. Precautions had therefore to be taken when measuring the concentrations of solutions of solutes whose colour is altered by change in pH. Solutions of alizarin in aqueous ethanol were found to change from pale orange to blue-red in colour after contact with the anodised foil. Sörensen[60] has noted the alteration of the colour of alizarin with pH and suggests its use as an indicator. Aqueous solutions

of Orange I changed colour from orange to red on treatment with the anodic film. In the case of these two compounds, in order to determine the amount of solute adsorbed by the film, the calibration solutions and those from which adsorption had taken place were made distinctly acid by the addition of 4 ml. of a 50% glacial acetic acid - 50% water mixture to 1 ml. of the solution before analyses were carried out.

(2) Estimation of the amount of aluminium in aqueous solution.

The concentrations of aqueous solutions containing aluminium were determined using "aluminon" reagent. This reagent forms a bright red lake with aluminium. It was prepared by dissolving 0.2g. of ammonium aurin tricarboxylate in 100 ml. of distilled water. Small concentrations of aluminium (up to 0.05mg. in 50 ml.) give pink to red coloured solutions which are suitable for colorimetric estimation.

The method of estimation used is described by Vogel[61]. 8 ml. of 2% hydrochloric acid, 10 ml. of 25% acetic acid and 5 ml. of the reagent were added to 2 ml. test solution, in that order. The volume was finally made up to 50 ml. by addition of a 10% solution of ammonium carbonate in 30% aqueous ammonia (0.880 S.G.) solution. The colour produced was compared on the Hilger "Spekker" adsorptiometer with that of standard solutions prepared by dilution of an aqueous solution containing 1.759g. "Analar" potassium aluminium sulphate per litre, of which 1 ml. contained

0.1 mg. of aluminium.

Measurement of Diffusion of Sulphonated Azo-compounds in Solution.

The porous plate method of Northop and Anson[62] was employed to measure the diffusion coefficients of compounds in aqueous solution at several temperatures. The apparatus is represented diagrammatically in Fig.3. The two solutions between which diffusion takes place are separated by the porous plate of sintered glass about 4cm. in diameter and 2mm. thick. A detailed description of the use of the apparatus is given by Holmes and Standing[63].

The inner compartment was filled with a 0.02% solution of the compound under investigation and arranged so that the porous plate was just below the surface of the distilled water in the outer compartment. The apparatus was then placed in a thermostat for 8 hours in order that thermal equilibrium might be attained and also to ensure that there was a steady concentration gradient through the porous plate. The external solution was then replaced by distilled water previously adjusted to the correct temperature. Diffusion was allowed to take place for a period of time, about 15 hours, measured from the time of addition of the distilled water to the external compartment, at the end of which a sample of the external solution was withdrawn and analysed colorimetrically.

The diffusion coefficient, D, was calculated from the equation overleaf.

$$D = \frac{2}{\lambda + 1} \cdot \frac{\beta}{t} \log_{10} \frac{C_0}{C_0 - (\lambda + 1) C_1}$$

where C_0 = the concentration in the internal compartment at the start of the measured diffusion period and C_1 that in the outer solution at the end of the experiment; λ = the volume of the external solution / volume of internal solution (= 19.2 for the apparatus used; $\underline{t}$ = time of diffusion, and β = a constant depending on the characteristics of the cell[64]. The value of β was determined by measuring the diffusion of N/2 potassium chloride, for which $D = 17.7 \times 10^{-6}$ cm.^{2}/ sec. at 25°, and was found to be 71.8 cm.$^{-1}$ for the apparatus used.

RESULTS AND DISCUSSION.

SECTION I.

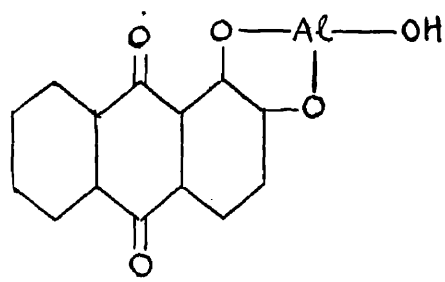
The Adsorption of Lake-forming Compounds.

It has already been mentioned (p.30) that dyestuffs capable of "laking" or forming co-ordinated complexes with alumina have been found to produce the most satisfactory dyed anodic films. A quantitative study was made of the adsorption behaviour of two lake-forming compounds, 1:2-dihydroxyanthraquinone (alizarin) and sodium, 1:5-diamino-4:8-dihydroxyanthraquinone-3:7-disulphonate (Solway Blue B, C.I. 1054).

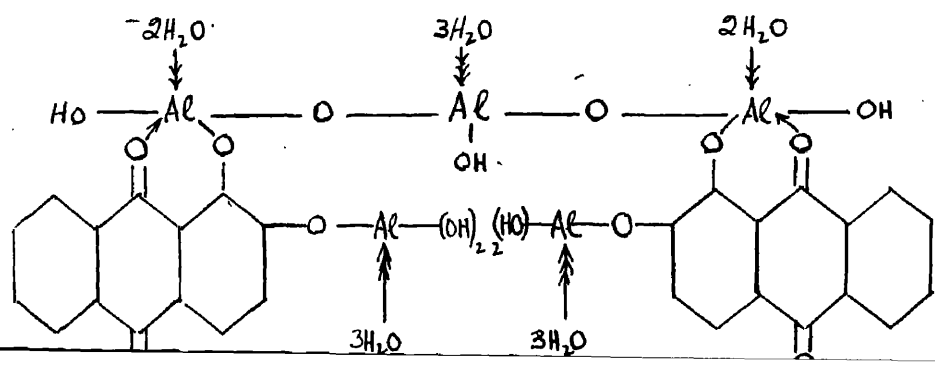
Adsorption isotherms plotted from the results of experiments with solutions of alizarin in an ethanol-water (60:40) mixture ranging in concentration from 0.4g./l. to 2.0g./l., at 59° and 51°, are shown in Fig.4. The coincidence of these isotherms, within the experimental error, demonstrates that the equilibrium adsorption values are independent of temperature. The adsorption process would therefore appear to involve the irreversible formation of a chelate complex between the alizarin and the anodic film. That the complex formed is very stable, is shown by the fact that when dyed films were subjected to prolonged treatment with water at the temperature of the adsorption experiments, no colour was removed, whereas some desorption has been found to occur under these conditions when the film is dyed with non-

chelating dyes.

The nature of the alumina-alizarin complex formed is uncertain. A considerable amount of work is reported upon the determination of the mechanisn of formation and structure of the aluminium-alizarin lake but doubt exists as to whether it is formed as a result of chemical combination or an adsorption process. Liebermann(65) suggested aluminium formed a compound with alizarin having the following structure:



Many subsequent authors have accepted this formula. Although Liebermann does not seem to have obtained a substance corresponding to it. Morgan and Smith(66) and Drew and co-workers(67) came to the conclusion that the metal is co-ordinately attached to the carbonyl and the adjacent hydroxy-group, while the hydroxy-group in the 2-position is sufficiently acidic for a further aluminium atom to become attached to it under suitable conditions, although this atom can be easily removed or replaced; thus they considered the aluminium-alizarin complex to have the following structure:



The evidence cited above indicates that the lake is a definite chemical compound but Williamson[68] disagrees with this view and states that the lake is an aluminium oxide-sodium alizarate adsorption complex. Weiser and Porter[69] studied the mechanism of formation of alizarin lakes with the hydrous oxides of iron, chromium and aluminium and concluded that the formation of lakes from sodium alizarate baths is due to adsorption of the dye anion by the oxide.

In view of the excellent fastness of anodic films dyed with alizarin, however, it would seem that the lake is more likely to be a chemical compound.

An attempt was made to throw some light on the structure of the lake by carrying out an absorptiometric titration of alizarin (1.0g./l.) in ethanol, with aqueous aluminium sulphate (1.0g./l.) The titration curve is shown in Fig.5. It was found that 1.5 ml. of the aluminium sulphate solution were necessary to complex the alizarin in 5 ml. of the alizarin solution. The ratio of aluminium atoms to alizarin molecules calculated from these figures is ca. 4.5:1.

If such a complex is formed between alizarin and the anodic film, it is difficult to visualise the orientation of the alizarin molecules with respect to the film. Determination of the orientation of adsorbed molecules on the film will be discussed in some detail in the section dealing with the adsorption of sulphonated

azo dyes, but here it may be stated that the results of equilibrium measurements for alizarin are consistent with the value for the surface area of the film (ca.12 x 10^5 cm.^{2}/g.), calculated from measurements with sulphonated azo dyes, if it is assumed that alizarin molecules form a close-packed monolayer in which they are attached to the film through the two hydroxy-groups in the 1- and 2- positions with the plane of the anthracene nucleus normal to the film surface.

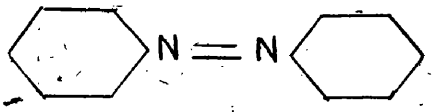
Isotherms plotted from the results of adsorption experiments carried out at 51°, 53.5°, and 58° with aqueous solutions of Solway Blue B, rangeing in concentration from 0.4g./l. to 2.0g./l. are shown in Fig.6. The isotherms reach maxima and subsequently fall, which may possibly be due to some dissolution of the aluminium-solute complex. Variation in temperature does not appear to affect the position of the isotherms greatly, they may in fact be considered to be independent of temperature within the experimental error, and the reaction is probably complex-formation as in the case of alizarin. In support of this, an estimation of the orientation of adsorbed molecules from the maximum adsorption value indicates that this dye also forms a close-packed monolayer on the surface, in which the molecules are oriented in a similar manner to those of alizarin, i.e. with the plane of the anthracene nucleus normal to the film surface. If adsorption were the result of reaction between the sulphonate groups and the film, the molecule would be expected to be flat on the surface (cf. p.67).

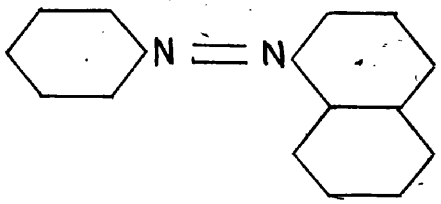
SECTION II.

Adsorption of Non-Chelating Solutes.

In order to find the part played by various functional groups in the adsorption of non-chelating compounds by the anodic oxide film, the adsorption of several compounds having similar basic skeletons but containing different functional groups was investigated. With a view to later work on the adsorption behaviour of sulphonated azo dyes the following basic skeletons containing the azo-linkage, and the functional groups listed, were selected for study.

Basic Molecules

(i) 

(ii) 

Functional Groups

(i) Hydroxy-group

(ii) Amino-group

(iii) Acetoxy-group

(iv) Methoxy-group

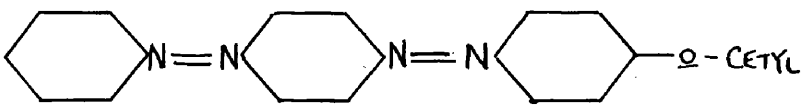
(v) Sulphonate-group

The adsorption behaviour of azobenzene itself was investigated in order to ascertain whether the contribution of the basic structure to the adsorption of substituted azobenzenes was of any significance.

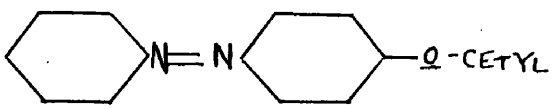
(1) The Adsorption of Azobenzene.

Adsorption experiments were carried out with solutions of azobenzene in dry benzene, absolute ethanol, and an ethanol-water (80:20) mixture. The results (Table 1) show that adsorption occurs only from aqueous ethanol, which suggests that water must take part in the attachment of the azobenzene molecule to the anodic film. It has been noted previously[70] that azobenzene is also adsorbed from solution in dry benzene (0.2g./l.) in presence of quinol (0.5g./l.)

An explanation of these results is suggested by the detection of several samples of hydrogen-bond cross-linkage of organic donor compounds in solution[71], or in monolayers on water[72], by bifunctional solutes such as water or quinol. It is well known that both the hydrogen atoms in the water molecule can simultaneously form bonds with different acceptors[73], this is best illustrated by the structure of water itself, and Rose[74] has shown that it is possible for one or both nitrogen atoms of an azo-group to take part in the formation of hydrogen bonds. Evidence that the azo-group has a slight but definite attraction for water has been found by Neustadter[75] when investigating the formation of monolayers on water. He found that of the two compounds having the following structures,

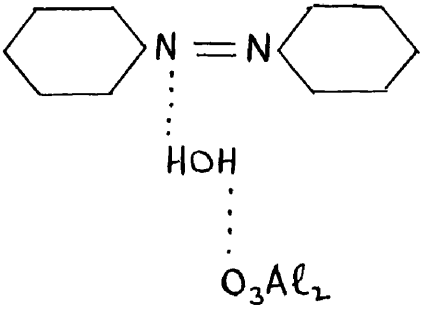


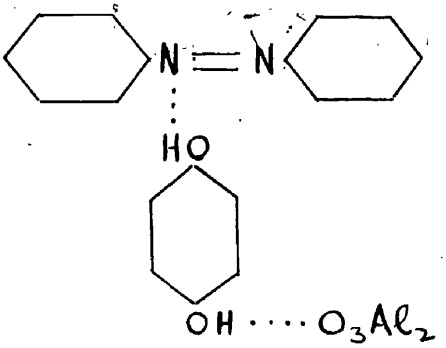
(i)



(ii)

(i) forms a monomolecular layer on water which (ii) does not. Thus it seems reasonable to conclude that the adsorption of azobenzene by the anodic film in presence of water or quinol takes place as shown below.



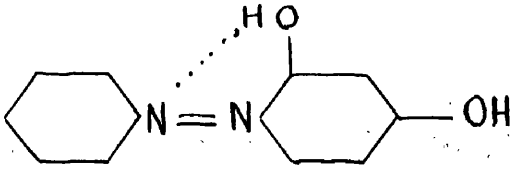


There is, however, another possible explanation for adsorption in presence of water. Some aluminium hydroxide may be formed by the water with the alumina of the film to which the azobenzene is directly attached by hydrogen-bonding through the hydrogen of the hydroxy-group. This seems unlikely on consideration of the structures of the monohydrates of alumina. Bernal and Megaw[76] have shown by X-ray powder photography that the two known monohydrates of alumina, böhmite (α-monohydrate) and diaspore (β-monohydrate), have the same structure, while Ewing[77] has shown the existence of an intramolecular hydrogen-bond in diaspore. Thus even if the hydroxide were formed, the hydrogen atoms in the molecule are unlikely to be free to form bonds with the nitrogen atoms of the azo-group in azobenzene. The results of an investigation of the effect of intramolecular chelated hydrogen atoms on adsorption are discussed in the next section.

(2) The Adsorption of Hydroxy-compounds.

The evidence of adsorption of azobenzene by hydrogen-bond cross-linkage with the anodic film suggests that the introduction of hydroxy-groups into the molecule may promote adsorption in solvents from which the parent compound is not adsorbed.

Experiments were carried out with solutions of 2:4-dihydroxy-azobenzene in adsolute ethanol, and the results (Table 2) show that the solute is adsorbed. It is likely that only the hydroxy-group in the 4-position is involved as that in the 2-position is intramolecularly chelated in a 6-membered ring as shown below.



In order to determine whether or not intramolecularly chelated hydrogen atoms have any effect on adsorption by the anodic film, the behaviour of two nitrated phenols, viz. o-nitrophenol and 2:4-dinitrophenol and of phenylazo-2-naphthol was studied. Mehta and Arshid[78] have shown that phenol itself is strongly adsorbed from aqueous solution, so that non-adsorption of the compounds chosen would almost certainly be a result of chelation. o-Nitrophenol and phenylazo-2-naphthol were not, as expected, adsorbed from aqueous solution, but the 2:4-dinitro-compound was found to be strongly adsorbed. Adsorption isotherms

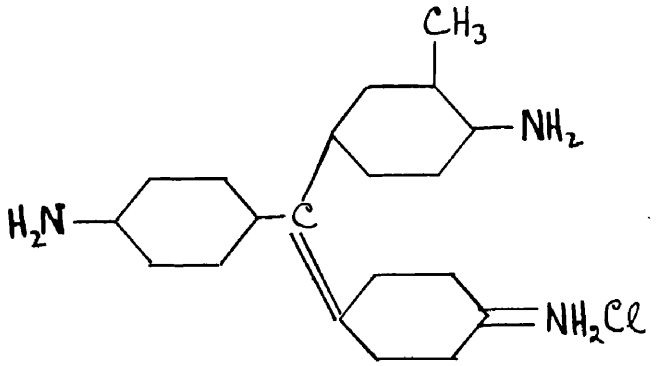
are shown in Fig 27. This result appears to show that the hydrogen of the hydroxy-group is more labile in this compound.

(3) The Adsorption of Amino-compounds.

The effect of the introduction of amino-groups into the basic azo-compound molecule was studied in the case of three compounds, 4-aminoazobenzene, phenylazo-1-naphthylamine, and phenylazo-2-naphthylamine. The results of qualitative experiments carried out with 4-aminoazobenzene showed that the solute was adsorbed from solution in dioxan but not from benzene. The two phenylazonaphthylamines were found to be adsorbed from carbon tetrachloride (adsorption isotherms are shown in Figs. 8 and 9), but the 2-isomer was not adsorbed from solution in benzene.

The importance of the solvent in the case of amino-compounds may be explained on the basis of work done by Arshid, Giles and Jain[79], which indicates that a number of intermolecular hydrogen-bond complexes formed between organic molecules in solution are more stable when the solvent is carbon tetrachloride or dioxan than when it is benzene or water. The applicability of this result to the adsorption of amino-compounds on the anodic film was tested by measuring the rates of adsorption of Magenta P (C.I.677),

whose formula is



from solution in dry dioxan, and dioxan-water mixtures (75:25 and 50:50). The rate curves obtained are shown in Fig.7. These curves show that the equilibrium amount adsorbed decreases from approximately 80 millimoles/kg. film, when the solvent is dry dioxan, to about 10 millimoles/kg. film, when the solvent contains 50% water. This appears to provide evidence that the behaviour of dioxan and water as solvents is as predicted from the work of Arshid et al.

An alternative explanation of this result may be put forward on the basis of the fact that the anodic film has been found to possess a positive surface change in presence of water[80]. Thus in the case of an ionised solute, the anion is attracted to the film by virtue of its opposite charge while the cation remains in solution. Basic dyes, having positively charged colour ions, therefore do not dye the film[70]. The decrease in the adsorption of Magenta P in presence of water may therefore be due to partial ionisation of the solute. As the zeta-potential of aluminium oxide-carbon tetrachloride and aluminium oxide-benzene interfaces has been found to be zero by Jensen and Gortner[81], this

explanation will not be valid in the case of the non-adsorption of amino-compounds from benzene.

The effect of intramolecular chelation can be determined from the isotherms of the two phenylazonaphthylamines. The 1-isomer has two hydrogen atoms available for bond formation where as the 2-isomer has only one. The affinities of these two compounds for the film were calculated from the equilibrium data assuming that they were adsorbed on specific sites in the anodic film. As discussed in the general introduction (page 10) the equation for this type of adsorption of an unionised compound is,

$$-\Delta\mu^{o} = RT \ln \frac{\theta}{1-\theta} - RT \ln (C)$$

where, θ = the fraction of the total number of available sites occupied, and (C) = the concentration of the solute in solution.

When $\theta = 0.5$, the affinity of the 1-isomer is found to be -0.38 kcal./mole and that of the 2-isomer -0.2 kcal./mole, both relating to adsorption at 50^{o}. The higher affinity of the 1-isomer suggests that both hydrogen atoms of the amino-group are involved in adsorption as compared with one in the case of the 2-isomer. Verification of this result was attempted by calculating the heat changes involved in the adsorption of both isomers. By applying the Clausius-Clapeyson equation to the equilibrium data at 49^{o} and 58^{o} for the 2-isomer, and at 36^{o} and 50^{o} for the 1-isomer the apparent heat of adsorption for the former was found to be

ca. -10 kcal./mole and that for the latter ca. -22 kcal./mole. These values may indicate the existence of one and two hydrogen bonds respectively between the solute and the film. They are much greater in magnitude than would be expected to accompany bydrogen bond formation, e.g. the heat of adsorption for phenol from aqueous solution on the anodic film, which may be considered to involve the formation of one hydrogen bond, has been calculated by Subramanian[70] to be ca. -4 kcal./mole.

Evidence that the apparent heat of adsorption on a given adsorbent appears to increase numerically with an increasing dissimilarity of structure between solute and solvent has been obtained for adsorption on nylon and wool by Chipalkatti, Giles and Vallance[82], who attribute it to entropy effects. This observation may explain the difference between the heats of adsorption of phenol from water and that of phenylazo-2-naphthylamine from carbon tetrachloride.

Comparison of the affinity of phenylazo-2-naphthylamine, 0.12 kcal./mole at 49°, with that of 2:4-dinitrophenol, 5.6 kcal./mole at 59°, suggests that a bond formed by the film with the hydrogen of a hydroxy-group is stronger than one formed with the hydrogen of an amino-group. The ease with which the adsorption of amino-compounds, but not that of hydroxy-compounds can be prevented by certain solvents leads to the same conclusion. In agreement with this, Flett[83] has found that the free energy

of formation of many intermolecular N...H...O bonds is lower than that of corresponding O...H...O bonds, in carbon tetrachloride solution.

(4) The Adsorption of Acetoxy-and Methoxy-compounds.

The evidence for the adsorption of both hydroxy-and amino-compounds shows that the presence of a substituent group capable of forming a hydrogen-bond promotes adsorption by the anodic film. It was therefore attempted to discover if adsorption could take place by the formation of bonds involving hydrogen attached to carbon.

Bonds are less readily formed by hydrogen attached to carbon than by hydrogen attached to nitrogen or oxygen, and a neighbouring group of powerful electron attracting nature is usually required to facilitate the reaction. Many workers have cited examples. Earp and Glasstone[84] detected bonding between oxygen in ether and hydrogen attached to aliphatic carbon activated by chlorine atoms or a negative group, e.g. a phenolic or nitrophenyl group.

The compounds chosen for study in the present investigation contained actoxy-and methoxy-groups. Solutions of 2:4-diacetoxyazobenzene in an ethanol-water (75:25) mixture were studied. Absorptiometric readings taken before and after treatment with the anodic film, at 60° and 33° for 36 hours and 48 hours respectively,

showed higher optical densities when read with light of wavelength 3300Å. Decomposition was suspected and U.V. spectra obtained for solutions of various concentrations before and after the experiment. These are shown in Fig.10 and seem to indicate that there is some of the dihydroxy-compound present in the final solutions. The fact that there is evidence of decomposition does, in itself, suggest that some form of close association of the solute and the adsorbent occurs. Alteration in the U.V. spectra of aqueous solutions of glycerol triacetate after treatment with the anodic film was also found (Fig.11).

Three tests with methoxy-compounds were carried out. Solutions of dimethylterephthalate in isooctane, 2:4-dinitroanisole in carbon tetrachloride, and 2-methoxynaphthalene in absolute ethanol were examined and in no case was adsorption found to occur. The behaviour of 2:4-dinitroanisole was similar to that of the acetoxy-compounds, i.e. the optical density of solutions read at the adsorption maximum for standard solutions was greater after contact with the anodic film. The U.V. adsorption spectra corresponding to standard and final solutions is shown in Fig.12., a slight shift in the maximum may indicate decomposition.

(5) The Adsorption of Sulphonated compounds.

Virtually all sulphonated azo dyes colour the film strongly, even those which contain no other groups capable of combining with the film, e.g., certain sulphonated tripheylmethane and o-hydroxy-

azo-compounds. The attraction in these instances must clearly be attributed to the sulphonic acid groups, and the non-adsorption of the simpler sulphonic acids, e.g. benzenesulphonic acid, naphthalene-1-sulphonic acid and naphthalene 1:5-disulphonic acid, and their sodium salts reported by Subramanium[70] must be a result of their high solubility in water, which reduces the affinity for the oxide film.

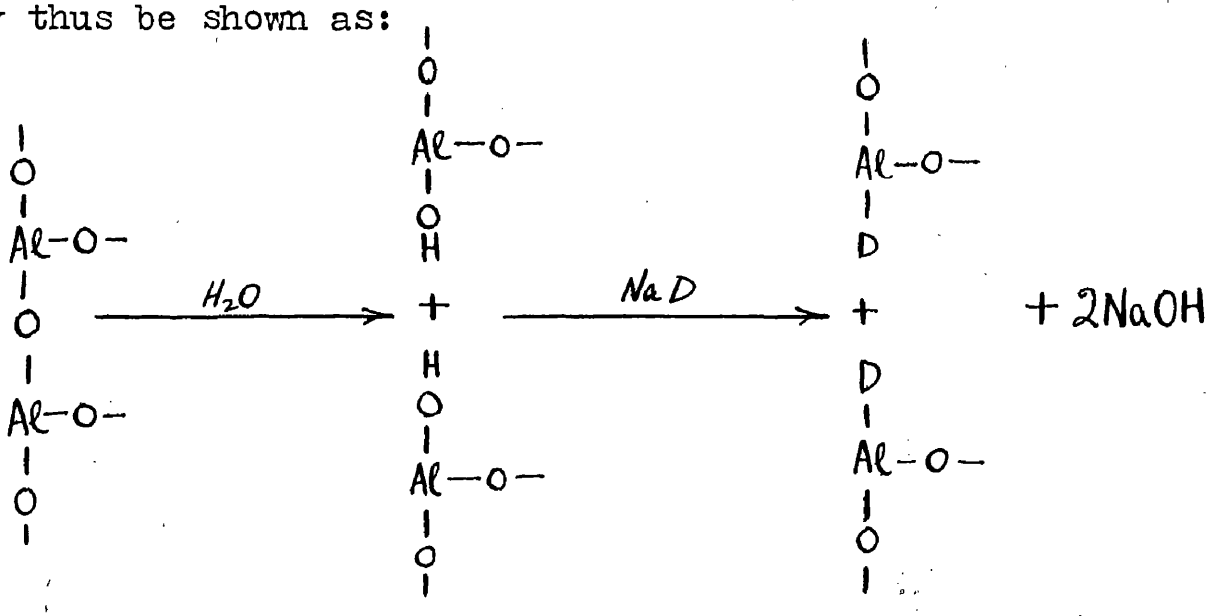
Sulphonated compounds based on the phenylazonaphthalene and naphthylazonaphthalene structures were studied, considerable adsorption and a measureable temperature coefficient being observed in every case (see e.g. Fig.14). The variation of the equilibrium data with temperature is evidence that adsorption is accompanied by a heat change which must represent a chemical reaction, probably the formation of a salt between the sulphonic acid group and aluminium.

The reaction between sulphonated compounds and the anodic film is probably similar in nature to the reaction of acids with alumina which has been investigated by Graham and Thomas[85]. They found that there is first a rapid conversion of surface hydroxy-groups to aquo-groups, followed by a slower complex formation between the acid anions and the metal, whereby the oxide structure is disrupted by breakage of hydroxy-and oxo-linkages. It is probable that sulphonated compounds react in this way also and may gradually penetrate the solid structure of the film.

Visable mechanical breakdown of the anodic film, which

loosens and can be easily rubbed off the basis metal, is sometimes found after it has been in contact with the sulphonated dyes for a considerable time. This occurs especially at the higher concentrations used, e.g. 2.0g./l., and with multibasic compounds, being most marked in solutions of the tetrasulphonated compound. Sky Blue FF (C.I.518), and supports the concept that reaction with sulphonates disrupts the oxide.

The reaction sequence in the adsorption of a sulphonated dye (NaD) may thus be shown as:



The existence of covalent bonds in the attachment of the dyes to the film appears to be confirmed by the impossibility of removing them by solvents, e.g. pyridine. It thus appears that only the organic anion is adsorbed by the film, the cations remaining in solution.

SECTION III.

The Effect of Molecular Structure on the Adsorption of Sulphonated Azo Dyes.

A detailed investigation of both the thermodynamic and kinetic aspects of the adsorption of sulphonated azo dyes from aqueous solution by the anodic film was carried out in an attempt to correlate their adsorption behaviour with their molecular structure. The effect of the following structural characteristics on adsorption was studied.

(i) The number of sulphonate groups in the dye molecule.

(ii) The disposition of the sulphonate groups.

(iii) The presence of other functional groups.

(iv) The presence of alkyl chains.

All experiments were carried out using 5ml. of test solution and an anodised strip ($3\frac{1}{2}$ x $\frac{1}{4}$ in.) as stated in the experimental section and which was found to be equivalent to a solution:oxide film weight ratio of 300:1, as it was discovered in the course of the work that the volume of solution used affected the position of the adsorption isotherms. This phenomenon is discussed in a later section (p.74).

(1) Adsorption Equilibria.

The nature of the isotherms.

The isotherms for all the sulphonated azo dyes studied were found to conform to one or other of the Brunauer et al. types I, II and V[86] which are shown in Fig.13. The experimental isotherms are shown in Figs. 14 to 21.

The isotherms for the three monosulphonates studied (Figs. 14,15 and 16) are all of type V. In the case of the polysulphonates they are of type I (Figs. 18 to 21) with the exception of those for the two disulphonates, aniline→R-acid and dodecylaniline→R-acid for which the isotherms (Fig.17) are of type II. There is evidence, however, that the shape of the isotherm is not a simple function.of the molecular structure of the solute. 1-Naphthylamine→R-acid, whose structure is very similar to those of the two disulphonates yielding type II isotherms, is adsorbed in accordance with the type I isotherm (Fig.19). Further, the results of work on the effect of the volume of solution on the position of the isotherm discussed later (p.74), show that at higher solution:oxide film weight ratios than that employed in the work discussed here, the isotherms for monosulphonates are of type II (Figs.23 and 24) whereas at the standard ratio (300:1) they conform to type V.

The exact relationship of the isotherm data to the dimensions of a completed monolayer in adsorption from solution is somewhat

uncertain[87] but adopting the Langmuir conception that the dye anions are adsorbed on fixed adsorption sites and are subject to neglible forces of attraction and repulsion in directions parallel to the film surface, it may be assumed that the plateaux in isotherms of types I and V represent approximately a completed monolayer, (cf.[88]).

The type II isotherm is more difficult to interpret satisfactorily. As adsorption in the case of sulphonates is the result of a chemical reaction between the aluminium in the film and the sulphonate group, multimolecular layer formation would not appear to be possible. Hence, the upper part of the type II isotherm, which does not attain a limit, must represent a progressive breakdown of film structure resulting from the adsorption reaction. It may be suggested that as a result of the nature of this reaction (see p. 60) all sulphonates should be adsorbed in accordance with this isotherm, but insufficient experimental evidence is available to come to any conclusion on this point. Perhaps this form would be obtained if the solutions could be made sufficiently concentrated.

The part of the type II isotherm corresponding to a monolayer was assumed to be that which is parallel to the X-axis for the two disulphonates whose adsorption was of this type. This assumption appears to be justified on the basis of the monolayer capacities calculated from the Brunauer, Emmett and Teller[89] equation

applied to the type II isotherms for Orange I adsorbed at various solution:film weight ratios (p. 77). This shows that the monolayer is represented by the commencement of the linear portion of the "knee" in these isotherms (Fig.23). The data calculated for these disulphonates on this basis give values for the specific surface area of the film which are consistent with those obtained from the equilibrium data of other dyes having more easily interpreted isotherms (see Table 3).

The orientation of adsorbed anions.

In order to determine the orientation of the dye anions adsorbed in a monolayer on the surface of the anodic film knowledge of three quantities is required.

(i) The monolayer capacity, i.e. the number of adsorbed anions comprising the monolayer.

(ii) The dimensions of the anions.

(iii) The surface area of the film available for the adsorption of the anions.

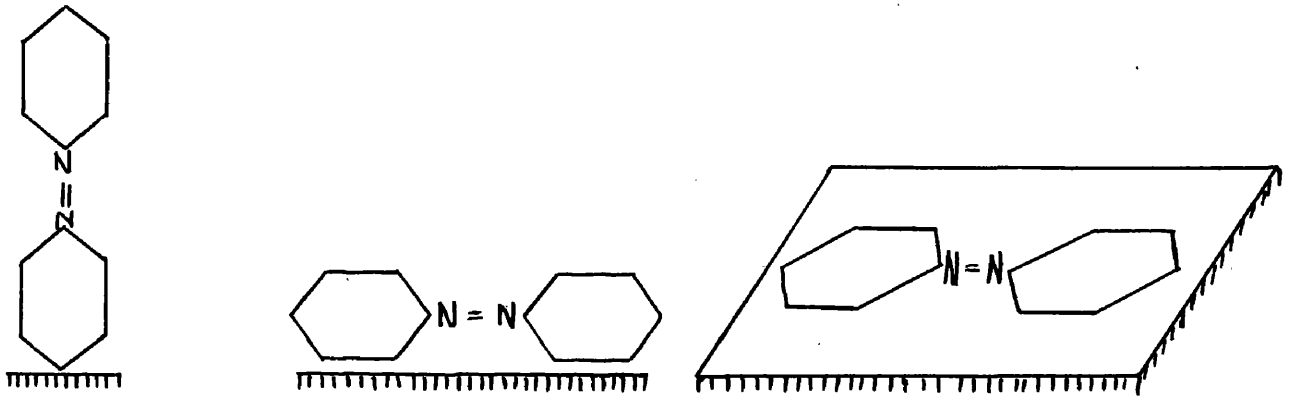
The monolayer capacity was determined from the experimental isotherms defining the part of the isotherm corresponding to a monolayer as discussed above. It will be noted that in all cases that the position of the isotherm varies with temperature. Thus the monolayer capacities are comparable only if they are referred to the same experimental temperature. All results in

Table 3 refer to equilibrium data obtained at 50°.

The dimensions of the anions studied were determined, in the absence of other means, by measuring the sides of the smallest rectangular box in which the anion could be enclosed, using Catalin (Stewart-type) scale models.

The surface area of the film available for adsorption of the anions was determined from the isotherms at 50° of Orange II (Fig.14). This compound was chosen as the reference compound because of its simple structure. The hydrogen of the hydroxy-group is intramolecularly chelated and thus will not take part in the attachment of the dye anion to the film. It is therefore reasonable to assume that the anion has only one point of attachment, i.e. at the sulphonate group, and the area occupied by it on the film may be taken as that measured when the anion is standing normal to the surface, with the sulphonate group at the lower end. The value of this area is 50Å, measured from the model. The surface area of the film was then estimated by multiplying the number of anions comprising the monolayer by the area of the anion, which gave a value of 12 $cm.^2/g. \times 10^{-5}$. This method of estimation does, of course, assume that there is a close packed monolayer at 50°(cf.[88]), but whether or not this is the case it may be assumed that under equilibrium conditions at any given temperature the same fraction of the total surface area of the film available for adsorption will be occupied by each dye.

The area occupied by the other anions was determined by dividing the specific surface area of the film obtained above by the number of anions in the monolayer. The values obtained were then compared with the cross-sectional area of the anion, measured from models, in the three positions shown below.



(i) (ii) (iii)

The three positions (i), (ii) and (iii) will henceforth be referred to as "end-on", "edge-on" and "flat" respectively. In Table 3 the values for the area of coverage of each anion calculated from its isotherms are compared with the area measured from the models in the three positions shown above. It will be seen from Table 3 that the area of coverage of the anions calculated from the isotherm data are reasonably consistent with those measured from models if the anions are oriented in the monolayer in accordance with the following general principles.

(i) The dye anions are attached to the film only through the sulphonate groups. The monosulphonate Orange I has a hydroxy-group free to form a bond with the film. If, however, both the

sulphonate and hydroxy-group were involved in the attachment of the anion to the film it would be expected that the anion would be oriented flat on the film surface. The value for this compound in Table 3 shows that this is not the case. Similarly the values for disulphonates having the two sulphonate groups situated at the same end of the molecule, viz. aniline → R-acid, dodecylaniline → R-acid and 1-naphthylamine → R-acid, indicate that the anions of these dyes are attached to the film only through the sulphonate groups.

(ii) All the sulphonate groups in the anions are involved in their attachment to the film surface. Thus in the case of the dyes sulphanilic acid → R-acid, Naphthalene Scarlet 4R, and Sky Blue FF, where the sulphonate groups are disposed more or less symmetrically around the molecule, the anions are oriented flat. The disulphonates Naphthalene Red EA and sulphanilic acid → 2-naphthol-6-sulphonic acid which have sulphonate groups at each end of the molecule also appear to be oriented flat.

(iii) Except in the case of the dyes mentioned under (ii) the anions are oriented at approximately right angles to the surface, probably because of the strong non-polar attraction between the hydrophobic residues of adjacent molecules. The dyes dodecylazo-geranine and dodecylaniline → R-acid which have long alkyl chains ($C_{12}H_{25}$) in the molecule appear to show this behaviour better than the corresponding dyes having no alkyl chains. This is probably

due to an increase in the non-polar attraction in the case of the former.

Thermodynamic Data.

(i) The change in chemical potential.

The change in standard chemical potential which is involved in the adsorption of each anion, and which is a quantitative measure of the affinity of the dye for the anodic film, was calculated using an adaptation of the equation discussed in the general introduction (p.7) for the adsorption of a dye, Na_zD, which is ionised in both the solution and adsorbent phases the ions being adsorbed on separate independent sites in the adsorbent, viz.,

$$-\Delta\mu^{\circ} = RT.\ln \frac{\theta_D}{(1-\theta_D)} \cdot \frac{\theta_{Na}}{(1-\theta_{Na})} - RT.\ln [Na]_s^z [D]_s$$

where θ_D and θ_{Na} are the fractions of the total number of sites available for the anion and cation respectively which are occupied at equilibrium, and $[Na]_s^z [D]_s$ is the expression for the activity of the dye in the solution at equilibrium.

If it is assumed that there are no specific sites in the film available for the adsorption of sodium ions, in accordance with the mechanism proposed to account for the adsorption of sulphonated compounds (p.60), the equation for the affinity of

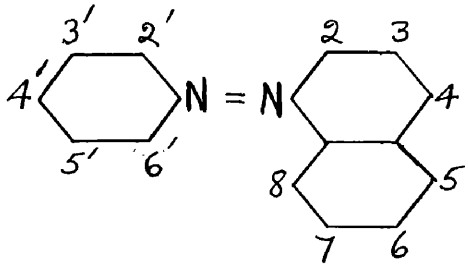
the dye reduces to,

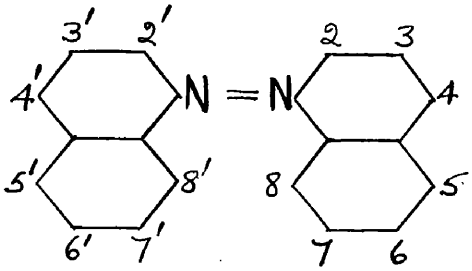
$$-\Delta\mu^{o} = -RT.\ln [Na]_{s}^{z} [D]_{s}$$

the standard state in the film being that when half the sites available for the adsorption of anions are occupied, i.e., when $\theta_{D} = 0.5$.

The values of the affinities for the various dyes calculated using this equation given in Table 4.

An explanation of these values can be suggested on the hypothesis that each sulphonate group contributes a proportion of the affinity and that this proportion is dependent on the position of the group in the dye molecule and that the separate effects of each group are additive. We may conveniently designate the affinity due to a sulphonate group in a given position in the molecule as the "partial affinity". Considering the results in Table 4 which refer to dyes based on the phenylazo- and naphthylazonaphthalene nucleii shown below.





The affinity values for the two monosulphonated dyes Orange II and Orange I in which the sulphonate group is in the 4′-position of the phenylazonaphthalene nucleus, are -8.8 kcal./mole. and -9.7 kcal./

mole. respectively. The higher value corresponds to the dye having the free hydroxy-group.

For the monosulphonate Naphthalene Red J the value of the affinity is -8.8 kcal./mole. This is the same as that for Orange II the addition of another condensed benzene ring to the molecule apparently having no effect on the affinity. Thus in the absence of other functional groups capable of taking part in the adsorption process the partial affinity of a sulphonate group in the 4 position of the two basic skeletons under discussion may be taken as approximately -9.0 kcal./mole.

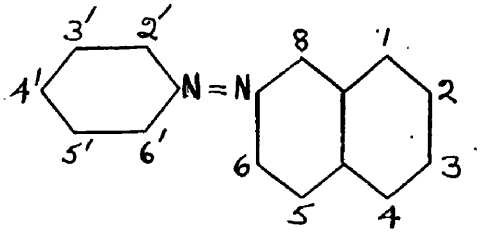
The disulphonate Naphthalene Red EA having sulphonate groups in the 4- and 6- positions of the naphthylazonaphthalene structure is found to have an affinity value of -13.4 kcal./mole. Now if we assume that this represents the sum of the partial affinities of the two sulphonate groups, the value for the sulphonate group in the 6- position is -4.5 kcal./mole. Hence any dye sulphonated in the 4- and 6- positions only should have an affinity for the film of value -13.5 kcal./mole. In fact the value found for the affinity of the dye sulphanilic acid ⟶ 2-naphthol-6-sulphonate is -13.1 kcal./mole., in good agreement with prediction.

Applying these principles to the dye aniline ⟶ R-acid the partial affinity of the sulphonate group in the 3-position should be -13.2 kcal./mole. Thus the affinity of the dye sulphanilic acid ⟶ R-acid for the film would be predicted as approximately -26.5 kcal./mole., which again is in good agreement with the

experimental value of -26.2 kcal./mole.

These results therefore appear to confirm the validity of the hypothesis of "partial affinities". The values thus calculated for the sulphonate groups in the various positions are given in Table 5.

As only two dyes having the basic structure,



i.e. dyes Azogeranine and Dodecylazogeranine, were examined the partial affinities for the two sulphonate groups in them could not be deduced.

The effect of the presence of the long alkyl chain, ($C_{12}H_{25}$), on the affinity of sulphonated azo dyes for the film is not very clear. Comparing the results for dyes aniline ⟶ R-acid and dodecylaniline ⟶ R-acid given in Table 4 it will be seen that the alkylated dye has approximately the same affinity as the unalkylated dye whereas comparison of the dyes Azogeranine and Dodecylazogeranine shows that the alkylated dye exhibits a considerably higher affinity. It might be expected that the presence of an alkyl chain would enable a dye to form a condensed monolayer more readily on account of increased surface activity and the affinity would therefore be higher than for the corresponding unalkylated dye, but the experimental evidence for this is not very consistent.

It has however, been observed that the dye dodecylaniline ⟶ R-acid behaves anomalously in photochemical degradation experiments[90], while this dye alone has a positive apparent entropy change on adsorption on the film(Table 4). Thus it appears that this dye does not conform to the general behaviour of dyes of its class which may be a result of its tendency to exist in solution as micelles, owing to the ease with which its conpact planar molecules can associate.

(ii) The apparent heat of adsorption.

The apparent heats of adsorption of several sulphonated azo dyes obtained by applying the Clausius - Clapeyron equation to the equilibrium data measured at two temperatures are shown in Table 4. It has been noted (p.11) that these values represent the algebraic sum of the heat changes accompanying two successive processes, (i) the removal of the solute from solution, and (ii) the attachment of the solute to the adsorbent. Even so, it is permissable to use the values obtained for comparative purposes where the adsorption systems contain the same adsorbent and solvent but different solutes, as in the present case.

It is clear from the results in Table 4 that correlation between the molecular structure of the dyes and their heats of adsorption is not possible. The mono- and disulphonates studied are adsorbed with an evolution of ca.8.0 kcal/mole, while for the tri- and tetrasulphonates the value is ca.12.0 kcal./mole. The

dye dodecylaniline ⟶ R-acid has a very large apparent heat of adsorption (-32.0 kcal./mole); the wide difference between this and the values for the other dyes may perhaps be attributable to the marked tendency of this dye to form micelles, but no work has been carried out to check this point.

(iii) The apparent entropy of adsorption.

The values of the apparent entropy of adsorption for several sulphonated azo compounds calculated from the equation,

$$\Delta\mu^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

are shown in Table 4. The significance of this parameter has already been discussed (p.12). Except for the dye dodecylaniline ⟶ R-acid the values are all negative which indicates that an ordered arrangement of the anions adsorbed on the film surface takes place, as would be expected. It appears that the numerical value of the entropy change generally increases with increasing sulphonation of the dye molecule but other than this no conclusion can be drawn regarding the effect of molecular structure on the entropy change.

The adsorption of dodecylaniline ⟶ R-acid is accompanied by a large positive entropy change which suggests that in this case the system becomes less ordered when adsorption occurs. A

possible explanation of this is that the dye can form stable micelles in solution in which the arrangement of the molecules is highly ordered.

The Effect of the Volume of Solution on Adsorption Eqilibria.

Comparison of isotherms obtained by Mehta[78] for the adsorption of Orange I by the anodic film (Fig.22) with that obtained by the author for the same compound (Fig.15) at a comparable temperature shows that very much greater adsorption of this compound was obtained by Mehta. The adsorption procedure followed by Mehta differed from that employed in the present work in two respects.

(i) The agitation of the tubes containing the experimental system was effected by horizontal, reciprocating shaking of the tubes and not by tumbling as in the present work.

(ii) The solution: film weight ratio employed by Mehta was 1250:1 compared with 300:1 in the present work.

The mode of agitation only affects the rate at which equilibrium is attained and not the actual equilibrium distribution of the system, provided sufficient time is allowed for attainment of equilibrium. Thus it is clear that the mode of agitation has no effect on the equilibrium data.

In order to determine if the discrepancy between the two sets of results was due to the different solution: film weight ratios

employed, experiments were carried out with Orange I using solution: film weight ratios of 2500:1, 1250:1, and 133:1 at 59°, the isotherms obtained are shown in Fig.23. It is clear from these results that the amount of adsorbed solute in equilibrium with a given concentration in solution varies considerably with the solution: film weight ratio used. Further data were obtained for the dyes Orange II, 1-naphthylamine ⟶ R-acid and sulphanilic acid ⟶ R-acid at various ratios. The isotherms for these compounds are shown in Figs. 24, 25, and 26 respectively and closely follow the pattern of those for Orange I. The effect is not confined to the adsorption of sulphonated compounds because it is shown in the case of aqueous solutions of 2:4-dinitrophenol (Fig.27).

In all cases it will be seen that the amount of the solute adsorbed increases with increase in the solution: film weight ratio employed. This suggests that the specific surface area of the film is greater at higher ratios. The surface area for each ratio was therefore calculated from the isotherms of the sulphonated compounds, as described in the section on the orientation of adsorbed anions on the film (p.64), assuming that the anions are oriented in the same manner at all solution: film weight ratios (cf. comments above for experiments at the 300:1 ratio).

It has been mentioned already that the exact portion of the type II isotherm corresponding to a monolayer is difficult to

determine. In the case of isotherms of this type obtained for the adsorption of the dyes aniline ⟶ R-acid and dodecylaniline ⟶ R-acid (Fig.17) there are clearly-defined horizontal portions which were taken to represent the existence of a monolayer, but the isotherms for Orange I shown in Fig.23 are difficult to interpret and the monolayer capacity cannot be read from them with any degree of confidence. To determine the monolayer capacities in this case use was made of the well-known equation derived by Brunauer, Emmett and Teller[89], usually known as the BET equation. This equation is based on a generalisation of the Langmuir mechanism of adsorption, but whereas the Langmuir equation applies only to type I isotherms, the BET equation claims to cover all five types of adsorption.

The BET theory retains the Langmuir conception of fixed adsorption sites, but allows for the formation of an adsorbed layer more than one molecule thick. The equation for the adsorption of gases is:

$$\frac{p}{x(p_o - p)} = \frac{1}{x_m c} + \frac{(c - 1) \cdot p}{x_m c \quad p_o}$$

where p = the pressure of the gas in equilibrium with x adsorbed molecules, p_o = the saturated vapour pressure, x_m = the monolayer capacity and c = a constant.

A plot of $\frac{p}{x(p_o - p)}$ against $\frac{p}{p_o}$ should therefore give a

straight line of slope $\frac{(c-1)}{x_m c}$ and intercept $\frac{1}{x_m c}$. Hence by measuring the slope of the line and the intercept, the monolayer capacity, x_m can be evaluated.

In the case of the adsorption of Orange I from aqueous solution, the pressure, p, was replaced by the concentration of the dye in solution, and p_o by the solubility of the dye in water at 59°, i.e.

$$\frac{[D]}{x([D]_S - [D])} = \frac{1}{x_m c} + \frac{(c-1)}{x_m c} \cdot \frac{[D]}{[D]_S}$$

where $[D]$ = the concentration of the dye in solution in equilibrium with x adsorbed molecules, and $[D]_S$ = the solubility of the dye in water.

The plots of $\frac{[D]}{x([D]_S - [D])}$ against $\frac{[D]}{[D]_S}$ are shown in Fig.28, for the isotherm data obtained at three solution: film weight ratios for Orange I. These plots are linear over a limited range of $\frac{[D]}{[D]_S}$ values and the monolayer capacities calculated from their slopes and intercepts are 700, 410, and 120 m.mole/kg. for the three ratios 2500:1, 1250:1 and 133:1 respectively. Examination of the isotherms in Fig. 23 shows that these values correspond approximately to the commencement of the linear portion of the "knee" in each isotherm.

The values for the surface areas of the film at each of the solution: film weight ratios employed were calculated from the results of all four sulphonated azo dyes studied. The results are shown in Table 6. The consistency of the values calculated from the data of each dye at a given ratio are added evidence that the orientation of adsorbed anions is as suggested by the evidence discussed previously (p.66). The surface area increases with increasing solution: film weight ratio and Fig.29 is a plot of the average surface area of the film, from the results in Table 6, against the number of ml. of solution/kg. film used. It appears from this curve that the value of the surface area of the film may reach a maximum at very high solution: film weight ratios.

An explanation of this phenomenon is suggested by the fact that the anodic film was found to be slightly soluble in water. A series of experiments was carried out under conditions identical to those obtaining in the adsorption experiments discussed above, by using distilled water in place of dye solution in order to determine the relationship between the amount of film dissolved and the solution: film weight ratio. The aluminium content of the water after contact with the anodised foil was determined by means of "aluminon" reagent as described on p. 42 and the amount of film corresponding to this calculated. The results of these experiments are shown in Table 7 and show that , as would be expected, the higher the solution: film weight ratio, the greater is the amount

of film dissolved.

The relationship of the percentage of the film dissolved to the specific surface area of the film at each solution; film weight ratio is shown in Fig.30. The curve shows that the surface area increases almost linearly with the percentage of the film dissolved. This fact suggests that the effect of increasing adsorption with increasing solution:film weight ratios is a result of an increase in the surface area of the film due to some of the original surface being dissolved.

Consideration of the porous structure of the film leads to the possible explanation that the effect of solution of the film exposed to the dye solutions is to widen the pores in the film and allow greater penetration of the film by the dye anions. This explanation would only be valid if the original pores in the film are of such a size to restrict complete penetration by the dye when only very small amounts of film are dissolved i.e. at low solution:film weight ratios. Rummel[91] has calculated the diameter of the pores to be about 100Å, assuming them to be of circular cross-section, which is of the same order as the dimensions of the dye anions under consideration thus increase in the pore diameter resulting from solution of the film may account for the greater adsorption observed at higher solution:film weight ratios.

(2) Kinetics of Adsorption.

Rate of adsorption isotherms.

The rates of adsorption at three temperatures were determined for each one of a series of sulphonated azo dyes, as described in the experimental section (p.39). The series of rate isotherms for the adsorption of Orange II, shown in Fig.31, are typical of those obtained for all the dyes studied.

It can be seen from Fig.31 that the rate of adsorption increases with rise in temperature. This is invariably found to be the case for adsorption processes[13] and is the result of the combined effect of heat on the velocity of the reaction between the dye and the film, and on the degree of aggregation of the dye in solution. It has been noted previously[92] that the size of adsorbate molecules has a considerable effect on their adsorption by an adsorbent having long and very narrow pores. The pores in the anodic film are in this category and hence the size of the dye molecules might be expected to influence the rate of adsorption if diffusion in the pores of the film is a controlling factor.

The form of the kinetics.

By analogy with the adsorption of dyes by fibres, the adsorption of sulphonated azo dyes by the anodic film will take place in three stages viz.

(i) Diffusion of dye anions through the solution to the anodic film surface.

(ii) Adsorption on the outer surfaces of the anodic film.

(iii) Diffusion inside the pores of the anodic film.

Under the experimental conditions obtaining, which include vigorous agitation of the system, it seems unlikely that (i) will be the rate-controlling stage (ii) will occupy negligible time compared with the diffusion processes.

Evidence that diffusion in the pores of the film is of great importance is provided by the fact whereas the geometrical external surface area of the film is 7.5 $cm.^2/g. \times 10^{-2}$, that determined from the equilibrium adsorption data for Orange II is 12.0 $cm.^2/g. \times 10^{-5}$, which indicates that a very large proportion of the anions adsorbed at equilibrium are inside the pores of the film. The results of the study of the effect of solution:film weight ratio on adsorption indicate that the pore-size of the film is comparable to the size of the dye anions under investigation (p.79) and this together with the fact that the dye anions will be subject to considerable forces of restraint in their passage along the pores suggests that (iii) will be by far the slowest of the three stages.

In order to discover whether or not the rate of adsorption of dyes by the film is in fact controlled by diffusion in the pores of the substrate, the applicability of Fick's Law to the rate measurement experiments was tested. The equation used was

derived by Hill[10] to describe the diffusion of a solute into a semi-infinite solid,

$$A = 2C.\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}$$

where A = the total amount of solute diffusing across unit area of boundary in time $\underline{t}$ from a solution of concentration C, and D = the diffusion coefficient.

The plot of A against $\underline{t}^{\frac{1}{2}}$ should therefore give a straight line whose gradient is proportional to $D^{\frac{1}{2}}$, assuming that D is independent of concentration and C is constant.

The results of rate measurements for the dyes studied all give straight lines when plotted on this basis, (Figs. 32 to 45) which shows that the adsorption of these dyes by the film follows a normal process of diffusion, at least in the early stages of adsorption. This indicates that the concentration C must remain constant throughout the adsorption, although the concentration of the dye in solution is actually decreasing with time. Speakman and Smith[93] observed similar behaviour in the case of the adsorption of acid dyes by animal fibres and suggested that a layer of dye particles was rapidly adsorbed on the outer surfaces initially, from which diffusion into the substrate took place. This layer was maintained at constant concentration by circulation of the dye solution. Work on vapour phase adsorption on the porous particles of a zeolite mineral[94] and on carbon[95] has also suggested the formation of an initial surface layer prior to diffusion.

When the series of curves for each dye are extrapolated back, (broken lines in Figs 32 to 45 show extrapolations), they appear to originate from a point having a position x- co-ordinate in all cases.

This apparent origin lies within the range covered by the experimental points in the case of the dye Dodecylazogeranine (Fig.40) and it is interesting to note that at time periods shorter in duration than that required for the apparent origin to be reached the effect of temperature on the rate of adsorption is reversed. Thus in the earliest stage of the adsorption process the rate appears to decrease with rise in temperature. This may show that the rate in the earliest stages is dependent on the affinity of the dye for the film and may be the case for all the dyes studied. In view of the lack of experimental evidence, however, no conclusion can be drawn on this point.

The fact that the Fick's Law lines do not originate from the real origin suggests that in the earliest stage of adsorption, the process is not one of diffusion and that it may then be a formation of the surface layer only. On the basis of this hypothesis, the y- co-ordinate of the apparent origin indicates the amount of dye adsorbed on the outer surface of the film prior to diffusion, and the x- co-ordinate represents the time taken for this process. The co-ordinates of the origin for each dye are shown in Table 8. These results may be summarised as follows:

(i) In the case of the three dyes based on the naphthylazonaphthalene structure the amount adsorbed before diffusion commences, decreases with increase in the number of sulphonate groups as does the period which elapses prior to diffusion.

(ii) For a given dye, the addition of a C_4H_9 or $C_{12}H_{25}$ alkyl chain to the molecule results in an increase in the amount adsorbed prior to diffusion, cf. the results for dyes aniline ⟶ R-acid, butylaniline ⟶ R-acid, dodecylaniline ⟶ R-acid, Azogeranine, Butylazogeranine and Dodecylazogeranine, also aniline ⟶ H-acid and butylaniline ⟶ H-acid. The time elapsing prior to diffusion increases with increase in chain length except in the case of the dyes based on aniline ⟶ R-acid.

(iii) In the case of the three monosulphonates based on the phenylazonaphthalene structure, the amount adsorbed is larger when the hydroxy-group in the molecule is methylated and still larger when it is chelated with an adjacent azo-group, than when the dye has a free hydroxy- group. The time taken for the initial adsorption increases in the same sense as the amount adsorbed.

(i) and (ii) indicate that the larger is the unsulphonated residue in the dye molecule, the greater is the amount adsorbed by the initial adsorption process. This suggests that the surface activity of the dye governs the initial adsorption. Consideration of (i),(ii) and (iii) leads to the conclusion that the solubility of the dye may be of importance in determining both the period of

time occupied by the initial adsorption process and the amount of dye adsorbed.

The fact that for three dyes, aniline ⟶ R-acid, aniline ⟶ H-acid and butylaniline ⟶ H-acid (Figs. 35, 44 and 45), the apparent origin has a negative y-co-ordinate cannot be satisfactorily explained along the lines indicated above. The Fick's diffusion lines - x-axis intercepts can only be interpreted as showing that for a short initial period of time no dye anions are adsorbed. Since the anodic film is positively charged it is highly unlikely that this time period corresponds to the adsorption of sodium ions although this is, in fact, what the intercepts appear to indicate.

Since, however, the above summary is confined to trends in series of results rather than to absolute values, it seems permissable to reach the conclusion that qualitatively the position of the apparent origin is determined to some extent by the surface activity and/or the solubility of the dye.

Activation energies of diffusion.

If the process of diffusion in the pores of the anodic film is one of activated diffusion, it is to be expected that the diffusion coefficient should vary with temperature according to the equation, overleaf.

$$D_T = D_o \cdot e^{\left(\frac{-E}{RT}\right)}$$

where D_o = a constant, and E = the activation energy.

To determine E, the logarithms of the slopes of the curves showing the amount adsorbed against the square root of time, were plotted against the reciprocal of the absolute temperature. The results for the dyes studied plotted on this basis are shown in Fig. 46 to 50 the gradients of these lines give the values of the activation energy required for the diffusion of the dyes into the anodic film and are shown in Table 9.

It might reasonably be expected that the activation energy of diffusion of a dye in the pores of the film would be higher than that in aqueous solution, as has been found in the case of large dye molecules penetrating into fibres, where the activation energy is about 10-30 kcal./mole[93]. In the present case (Table 9) the activation energy of diffusion is ca.-10 kcal./mole for most dyes. The value for the dye Naphthalene Red J, however, is only -4.0 kcal./mole, which is comparable to that for the diffusion of dyes in water (Table 10). It has been observed by several workers that diffusion in solids does not invariably require large acfivation energies. Diffusion in fibres does however, seem to require a high activation energy. Kressman and Kitchner[128] have suggested that the reason for this lies in

the distortion of the flexible macromolecular structure by the diffusing molecules. With rigid porous solids on the other hand, where this does not apply, the activation energy for the diffusion of molecules smaller than the pores may be almost the same as for diffusion in an aqueous medium. Evidence that the dye molecules are sufficiently small to penetrate the anodic film to a considerable extent is provided by the fact that while its external surface area is of the order of 7.5×10^2 $cm^2/g.$, the surface area measured by the adsorption of sulphonated azo dyes is about 12×10^5 $cm^2/g.$

The results given in Table 9 may be summarised as follows.

(i) Considering the values for the three monosulphonates, Orange I, Methylated Orange I and Orange II, the activation energy falls when the hydroxy-group in Orange I is chelated or methylated, presumably there is then no hydrogen bond between this group and water to be broken before the dye is adsorbed.

(ii) The activation energy falls when the hydrocarbon residue of the dye is increased by the addition of:

(a) A benzene nucleus, cf. the dyes Orange I and Naphthalene Red J.

(b) A $C_{12}H_{25}$ alkyl chain, cf. the following pairs of dyes, aniline ⟶ R-acid and dodecylaniline ⟶ R-acid, Azogeranine and Dodecylazogeranine.

This reflects an easier removal of the dyes with the larger hydrocarbon nucleii from their aqueous environment.

(iii) The addition of a C_4H_9 alkyl chain results, however, in an increase in activation energy.

It is possible that this is a result of the formation of particularly stable aggregates of this dye in solution. In order to examine this hypothesis the diffusion of a series of three dyes in aqueous solution viz. Azogeranine and its C_4 and C_{12} homologues wasstudied. The diffusion coefficients were determined by diffusion through a porous plate (as described in the experimental section p.43) at three temperatures for each dye, and the activation energy of diffusion in solution measured from the gradient of the plot of the logarithm of the diffusion coefficient against the reciprocal of the absolute temperature. The plots for each dye are shown in Fig.51. and the values of the gradients in Table 10.

The results show that the activation energy of diffusion in solution decreases very slightly on addition of a C_4H_9 alkyl chain and decreases further when a $C_{12}H_{25}$ chain is added. Thus the addition of a C_4H_9 chain does not seem to lead to abnormal behaviour in solution.

It is interesting to note that there is no apparent correlation between the number or the positions of sulphonate groups in the dye molecule and the activation energy values in any way corresponding to that found for affinity values.

CONCLUSIONS.

The conclusions already given in the text are, for convenience summarised below

The results of adsorption experiments with two solutes capable of forming lakes with aluminium viz. alizarin and Solway Blue B, show that in both cases adsorption is independent of temperature and that desorption is not effected by treatment with water under conditions similar to those obtaining during adsorption. Thus it appears that the adsorption of these compounds involves the irreversible formation of very stable chelate complexes with the aluminium of the anodic oxide film.

Orientation measurements suggest that alizarin is attached to the film through the two hydroxy-groups in the 1- and 2-positions. Solway Blue B appears to be oriented in a similar manner, which indicates that the sulphonate groups in the molecule are not playing an important part in the adsorption of this compound.

The adsorption of solutes from dry organic solvents occurs only when there is a hydrogen atom in the molecule free to form intermolecular bonds. Thus hydroxy- and amino-compounds (from certain solvents) are adsorbed, presumably by the formation of hydrogen bonds with the oxide film. The dependence of the adsorption of amino-compounds on the solvent suggests that the N...H...O bond formed in adsorption has lower free energy than the O...H...O bond.

The adsorption of azobenzene, which is not adsorbed from dry solvents, is promoted by the presence of water. This appears to arise from the fact that the two hydrogen atoms in the water molecule can simultaneously form bonds. Hence a bond is formed between one hydrogen atom and a nitrogen atom of the azo-linkage in azobenzene and between the other hydrogen atom and an oxygen atom of the oxide film. Thus water forms a bridge linking azobenzene to the film.

Intramolecular chelation of hydroxy-groups prevents them taking part in attaching compounds to the film, even in presence of water, cf. phenol and o-nitrophenol. In the case of the amino-compound, phenylazo-2-naphthylamine, where one of the hydrogen atoms of the amino-group is intramolecularly chelated, adsorption takes place from carbon tetrachloride as there is still one hydrogen atom free to form an intermolecular bond. The affinity of this compound for the film is, however, much lower than that of the 1-isomer, which apparently forms two hydrogen bonds with the film.

The results of experiments with methoxy- and acetoxy-compounds designed to determine whether these compounds are adsorbed by the formation of a hydrogen bond with hydrogen attached to carbon, were complicated by suspected decomposition of the solutes. The fact that decomposition may occur does in itself suggest that some form of close association of these solutes and the film occurs.

The surface area of the film was found to increase when in

contact with increasing volume of aqueous solutions. This is evidently the result of small amounts of the film being dissolved in water and the surface was found to be almost linearly related to the amount of film dissolved. It is suggested that solution widens the pores of the film and allows greater penetration of solute molecules thus increasing the area available for their adsorption.

The adsorption of sulphonated compounds is accompanied by a measureable evolution of heat, which indicates that a chemical reaction, probably salt formation, takes place between the sulphonate groups and the film. This mechanism only involves the adsorption of the anion, which is initially attracted to the film surface by virtue of the positive charge possessed by the film in contact with water. Orientation measurements show that the adsorbed anions are oriented in such a manner that all their sulphonate groups are attached to the film.

The affinity of sulphonated azo dyes for the film appears to be the sum of the affinities of the sulphonate groups in the molecule, each contributing to the total affinity an amount characteristic of its position in the molecule. No contribution is made by the aromatic residue of the dye anion or by free hydroxy-groups, which form hydrogen bonds with the film in non-sulphonated compounds.

The apparent heat of adsorption does not appear to be closely

related to molecular structure but is generally higher for tri- and tetrasulphonates than for mono- and disulphonates.

The negative entropy change found to accompany adsorption shows the dye-film phase is more ordered than the dye-solvent phase, as would be expected from the orientation measurements. There is, however, no correlation between the numerical value of the entropy change and molecular structure other than a tendency to increase with increasing sulphonation of the molecule.

A study of the kinetics of the adsorption of sulphonated azo dyes by the film shows that the actual adsorption process takes place in two stages,(i) the building up of a layer of dye on the outer surfaces of the film followed by (ii) diffusion into the pores of the film. The extent of the initial process seems to be governed by the surface activity and/or solubility of any dye.

The activation energy of the diffusion process is lowest for dyes which are most easily removed from solution, e.g. dyes having intramolecularly chelated hydroxy-groups which cannot form hydrogen bonds with water require less activation energy to diffuse than similar dyes with free hydroxy-groups. The activation energy decreases with increase in the size of the aromatic residue and also on addition of a $C_{12}H_{25}$ alkyl chain, presumably for the same reason.

The fact that the activation energy is increased by the addition of a C_4H_9 alkyl chain cannot be satisfactorily explained on the evidence available.

PART II.

ADSORPTION ON CHROMATOGRAPHIC ALUMINA

INTRODUCTION.

The use of alumina in the field of chromatography has been well established and developed during the last twenty years. Adsorption columns are now a standard part of the equipment of organic chemists and more recently have been applied to inorganic analysis.

A great deal of experimental work is reported in the literature upon the effect of variations in a number of factors on the effectiveness of chromatographic adsorption on alumina, but the actual chemical mechanism of the process has been very little studied by any systematic and quantitative procedure.

The present work was accordingly undertaken, to follow up the conclusions of the adsorption studies on the anodic oxide film by determining whether similar forces are operative in adsorption on alumina powder. It is hoped that the results of static adsorption experiments may be of use in further work on the behaviour of dyes on alumina columns.

The adsorption properties of alumina vary according to its crystalline structure, its state of hydration, particle size and purity. Active alumina suitable for use as a chromatographic adsorbent is generally prepared by heating technical pure $Al(OH)_3$ (hydrargillite) for a few hours at ca. 400°. The crystalline form of alumina prepared in this way is the -modification which has a spinel lattice in which a third of the positions available for the

adsorption of the metal atoms are unoccupied[96]. Taylor[97] found that the adsorption activity of alumina, measured as the weight of dye (Waxoline Blue CS) adsorbed by unit weight of alumina, was directly related to the amount of δ-alumina present. The most stable form of alumina, α-alumina, which is the most compact form, having a hexagonal close-packed structure in which the aluminium atoms are regularly arranged[98], does not exhibit adsorptive properties[99]. It has been suggested[99] that in the adsorption of organic compounds from non-aqueous solution, certain points on the adsorbent particle (the so-called "active" points) play an important part. These occur mainly at positions where the crystal lattice is faulty, which may explain why the more ordered α-form of alumina, does not adsorb while δ-alumina is an effective adsorbent.

The Preparation and Standardisation of Alumina for Use as an Adsorbent.

Reichstein and Shoppee[100] have described a method of preparation of active alumina by heating $Al(OH)_3$ for about 3 hours, with stirring, at 380° to 400°. Such preparations always contain free alkali (or sodium carbonate) which may cause secondary reactions when the alumina is used as an adsorbent, e.g., condensation of ketones or aldehydes. Washing with dilute acid or water eliminates this risk and reduces the activity of the alumina.

The activity of alumina can be measured by the method of

Brockmann and Schodder[101]. They obtained alumina of five different grades of activity, which are differentiated by the behaviour on a column of a number of coloured azo compounds, viz., azobenzene, p-methoxyazobenzene, Sudan Yellow and Sudan Red, in order of adsorbability. The following table shows the behaviour of these compounds on alumina columns.

STANDARD	I	II		III	
SOLUTION CONTAINING	a + b	a + b	b + c	b + c	c + d
ADSORBED ON COLUMN TOP	b	b	c	c	d
BOTTOM	a		b		c
FOUND IN FILTRATE		a		b	

a = AZOBENZENE ; b = p-METHOXYAZOBENZENE ; c = SUDAN YELLOW

d = SUDAN RED

Alumina of standard I is completely activated by calcination, whereas the others are more or less deactivated by prolonged exposure to moist air. It has been found[102] that the addition of 3.3% water to a completely activated alumina gives it an activity of standard III. Alumina of only slightly varying adsorption properties is available commercially.

For adsorption in aqueous media the properties of alumina can be modified by washing with acid or alkali. The former is frequently used for the adsorption of dicarboxylic amino acids and acidic peptides[103] while both have been used in work on the

separation of inorganic ions.

Adsorption of Organic Compounds from Non-aqueous Solvents on Alumina.

Brockmann[99] investigated the effect of various functional groups on the adsorption sequence of p-substituted azobenzenes and stilbenes, from benzene and carbon tetrachloride respectively, on alumina columns. He found the following relationship between the firmness with which the derivative was adsorbed and the nature of the functional group.

Azobenzenes.

$R=C_6H_5N=NC_6H_4-$

-COOH
-OH
$-NH.COCH_3$
$-O.COCH_3$
$-NH_2$
$-O.COC_6H_5$
$-COOCH_3$
$-N(CH_3)_2$
$-NO_2$
$-OCH_3$
-H

Stilbenes.

$R=C_6H_5CH=CHC_6H_4-$

-COOH
$-CONH_2$
-OH
$-NH_2$
$-NH.COCH_3$
$-O.COCH_3$
$-COOCH_3$
$-N(CH_3)_2$
$-O.COC_6H_5$
$-NO_2$
$-OCH_3$
-H

The two series are in almost complete agreement with each other. Differences being found only in the behaviour of the groups, $-NH.COCH_3$, $-O.COCH_3$ and $O.COC_6H_5$. These are adsorbed in the same order in both cases, but the stilbene derivatives lie higher in the sequence than the corresponding derivatives in the azobenzene series.

Brockmann (loc. cit.) also studied the effects of the solvent, and of the acid or alkaline nature of the alumina, on the adsorption sequence of azo dyes and found that both these factors had a marked effect on it.

He suggested that the dependence of the adsorption sequence of the dyestuffs on the solvent is perhaps due to variations in the solvation of the hydroxy- and amino- groups present, and further that depending on the nature of the solvent, the dyestuffs are partly adsorbed in the azobenzene form and partly in the tautomeric quinone-imine form.

The adsorption sequence of dyes on acid and alkaline alumina found by Brockmann (loc. cit.) supported the observation made by Hesse and Sauter[104] that basic compounds are adsorbed better on alkaline alumina than on acid alumina, while acidic compounds show the opposite behaviour.

From the results of work on compounds whose adsorption is independent of these factors Brockmann (loc. cit.) concluded that the adsorption affinity of a compound is practically an additive

function of the adsorption affinities of the basic skeleton and of the functional groups but only when there is no possibility of tautomerism and when solvation by the solvent does not occur. Strain[105] has drawn similar conclusions from work on the adsorption of carotenoids. These conclusions are,however, based largely on qualitative work.

The forces operative in attaching solutes to alumina have been less intensively investigated. Hesse and Sauter[106] infer that azobenzene is adsorbed by the operation of van der Waals forces, while basic and acidic dyes appear to form complexes with the oxide. The importance of hydrogen-bond formation in the adsorption process has been demonstrated by Hoyer[107] who has shown that α-hydroxy- and α-amino-anthraquinone are less strongly adsorbed on silica and alumina than the β-isomers from benzene solution. He attributes this result to the fact that intramolecular hydrogen-bonding occurs in the α-isomers whereas in the β-isomers, the hydrogen atoms of the functional groups are free to form intermolecular bonds.

Adsorption of Inorganic Ions on Alumina.

A considerable amount of work has been done on the separation of inorganic cations and anions on alumina columns but theories suggested to account for their adsorption by various authors are somewhat divergent.

The fact that sodium ions are generally present in technical

alumina led Schwab and Jockers[108] to suggest that the adsorption of cations depended upon an ion-exchange process between the sodium ions on the column and the cations in solution. Flood[109] from his work on alumina impregnated paper reached the same conclusions. Fricke and Neugebauer[110], however, from work on sodium-free alumina prepared from aluminium foil, concluded that the presence of sodium ions is not necessary for adsorption. Other workers have supported this conclusion[111]. Other theories which explained the adsorption process on the basis of the precipitation of basic salts caused by the alkaline reaction of technical alumina[112] and precipitation of basic carbonates due to alkali carbonates and bicarbonates being present[113] have been put forward. From a study of the adsorption of cations and anions from aqueous solutions of cuprous chloride, Jacobs and Tompkins[114] found that both ions were adsorbed, but the cation was more strongly adsorbed than the anion. They concluded that alumina functioned as an amphoteric ionic adsorbent which engages in both hydrogen ion/cation and hydroxyl ion/anion exchange. The non-equivalence of the adsorption of cations and anions is attributed to additional sodium ion/cation exchange. They suggested that this was associated with the presence of sodium aluminate as impurity in the alumina and was not due to hydrolytic adsorption nor to an exchange involving aluminium ions or hydrogen ions. The same authors[115] have also suggested the possibility

of molecular adsorption taking place together with additional ion exchange between the sodium ions and cations.

Sacconi[116] considers that the major process whereby cations are adsorbed on pure alumina is one of hydrolytic adsorption associated with aluminium ion/hydrogen ion exchange. He suggests that the adsorption of inorganic salts may take place according to the following equations:

$$M^{++} + H_2O \rightleftharpoons M(OH)^+ + H^+ \qquad \text{(in solution)}$$

This reaction is displaced towards the right-hand side because of the lowering of hydrogen ion concentration by aluminium ion/hydrogen ion exchange, i.e. the surface buffering effect of alumina. The aluminium salt liberated is then adsorbed as a basic salt:

$$6M^{++} + 6H_2O \longrightarrow 6M(OH)^+ + 6H^+$$
$$Al_2O_3 + 6H^+ \longrightarrow 2Al^{+++} + 3H_2O$$
$$2Al^{+++} + 2H_2O \longrightarrow 2Al(OH)^{+++} + 2H^+ \text{ and etc.}$$

Since alumina is in excess, the process will continue until adsorption is complete. In support of the aluminium ion/hydrogen ion exchange hypothesis, Wagner[117] has shown that the dissolution of alumina in acids is a surface reaction depending on the concentration of other electrolytes present as well as on the hydrogen ion concentration. In the case of adsorption on technical alumina the sodium ion/hydrogen ion exchange process will be superimposed on the aluminium ion/hydrogen ion exchange.

Sacconi (loc. cit.) also found that the adsorption affinity is proportional to the polarising power exerted by the ions as well as to the polarisability of the groups co-ordinated around the ions; this conclusion was also reached by Venturello and Agliardi (118).

The adsorption of cations on basic alumina columns and of anions on columns previously treated with hydrochloric acid has been explained by Wieland(103) on the basis of ion exchange as follows. Treatment with hydrochloric acid results in the adsorption of chloride ions by the alumina which can be exchanged for organic or inorganic anions. By heating technical alumina, the alkali carbonate which it contains forms active centres of sodium aluminate. The sodium ions can then be exchanged with cations in solution and adsorption occurs.

Adsorption of Dyes on Alumina.

The adsorption of some synthetic dyes on alumina from solutions in water and ethanol was investigated by Ruiz, Chovin and Moureu(119) who concluded that the presence of hydroxyl or acid groups increased adsorption whereas amino-groups diminished it and that adsorption was modified by the orientation of the groups. They also found that the solvent had a definite effect on adsorption. In agreement with this Mutch(120) found that alumina freely adsorbs acid dyes but has little affinity for basic dyes and that

desorption was not readily effected by washing with water or organic solvents. The operative mechanisms of adsorption were not, however, determined.

EXPERIMENTAL.

Preparation of the Substrate.

The alumina used throughout the work was taken from a single sample supplied by Savory and Moore for chromatographic use. It was found to be alkaline in character; 20 ml. of distilled water shaken up with 1g., at room temperature, had a pH of 9.5. In view of the fact that a significant part of the work concerned the adsorption of acid dyes, which have been found to be unadsorbed by alkaline alumina[121], the powder was acidified before use.in This was done by washing 100 g. twice with 200 ml. 2N hydrochloric acid, followed by rinsing several times with water. It was then dried in an oven at 150° for several days. Under the same conditions as for the alkaline sample this alumina changed the pH of distilled water to 4.4.

The dry, acid alumina was standardised, according to the method of Brockmann and Schodder[101] (p.95), and its activity found to correspond to Brockmann's standard II. It was stored in a desiccator and standardised frequently during the course of the work, being maintained at standard II throughout.

Dyes and other Reagents Used.

The adsorption characteristics of the following compounds on acidified alumina were studied.

Unsubstituted azo-compounds.

(i) Azobenzene (ii) Bis(phenylazo)benzene

Pure samples of (i) and (ii) were obtained by recrystallisation of commercial samples.

Hydroxy-compounds.

(i) Phenol (iii) 2-Naphthol

(ii) Resorcinol (iv) 2:4-Dihydroxyazobenzene

Pure samples of (i), (ii) and (iii) were prepared from commercial samples by recrystallisation. (iv) was prepared as described on page 35.

Amino-compounds.

(i) p-Nitroaniline (iii) p-Aminoazobenzene

(ii) m-Nitroaniline (iv) Phenylazo-1-naphthylamine

(i), (ii) and (iii) were purified commercial samples. (iv) was prepared as described on page 35.

Miscellaneous compounds.

(i) 2:4-Diacetoxyazobenzene (iii) Cellobiose

(ii) Sucrose

(i) was prepared from 2:4-dihydroxyazobenzene by acetylation

in the normal manner.

(ii) and (iii) were pure commercial samples.

Sulphonated azo-compounds.

Sodium salts of the compounds listed below were used in every case and are referred to subsequently by the names given in parenthesis.

		Colour Index No.
(i)	Sulphanilic acid ⟶ 2-naphthol (Orange II)	151
(ii)	1-Naphthylamine-4-sulphonic acid ⟶ 2-naphthol (Naphthalene Red J)	176
(iii)	1-Naphthylamine ⟶ 2-naphthol-3:6-disulphonic acid (1-Naphthylamine ⟶ R-acid)	88
(iv)	1-Naphthylamine-4-sulphonic acid ⟶ 2-naphthol-6-sulphonic acid (Naphthalene Red EA)	182
(v)	Aniline ⟶ 1-acetylamino-8-naphthol-3:6-disulphonic acid (Azogeranine)	31
(vi)	p-n-Butylaniline ⟶ 1-acetylamino-8-naphthol-3:6-disulphonic acid (Butylazogeranine)	
(vii)	p-n-Dodecylaniline ⟶ 1-acetylamino-8-naphthol-3:6-disulphonic acid (Dodecylazogeranine)	
(viii)	Ditolyl-disazo-3:6-disulpho-2-naphthylamine phenetole (Congo Orange R)	459

		Colour Index No.
(ix)	p-Sulpho-o-toluene-azo-o-toluene-azo-2-naphthol-8-sulphonic acid (Ponceau 6RB)	286
(x)	Sulphanilic acid → 2-naphthol-3:6-disulphonic acid (Sulphanilic acid → R-acid)	
(xi)	1-Naphthylamine-4-sulphonic acid → 2-naphthol-6:8-disulphonic acid (Naphthalene Scarlet 4R)	185

Samples of compounds (vi), (vii) and (x) were prepared in the laboratory by diazotising the appropriate amine and coupling with the appropriate naphthol. In the case of (vi) and (vii) the naphthol was prepared as described on p.38.

Pure samples of all the other compounds were prepared from commercial samples by salting out from aqueous solution with sodium chloride, followed by recrystallisation from ethanol-water mixtures.

The purity of all the sulphonated azo-compounds determined by reduction with titanous chloride as described by Knecht[59]. All samples used in the experimental work were of over 95% purity as estimated by this method.

Adsorption Procedure.

The procedure employed to obtain equilibrium and rate data for the systems studied was similar to that used in the case of adsorption on the anodic oxide film (p.39). In the course of

the present work, however, it was found that the time required to attain equilibrium was very short and the procedure was modified accordingly (p. 122).

0.1g. dry acidified alumina was used with 5ml. test solution, giving a solution:oxide weight ratio of 50:1 compared with 300:1 in the case adsorption experiments on the anodic oxide film.

Analytical Techniques.

The determination of the concentration of solutions of the compounds studied was effected by photoelectric absorptiometry, except in the case of solutions of sucrose and cellobiose which were determined by measuring the refractive indices of the solutions on a Pulfrich refractometer. By measurement of the refractive index of a solution before and after treatment with alumina the difference in concentration, and thus the amount adsorbed, was determined.

RESULTS AND DISCUSSION.

SECTION I.

The Adsorption of Non-sulphonated Compounds.

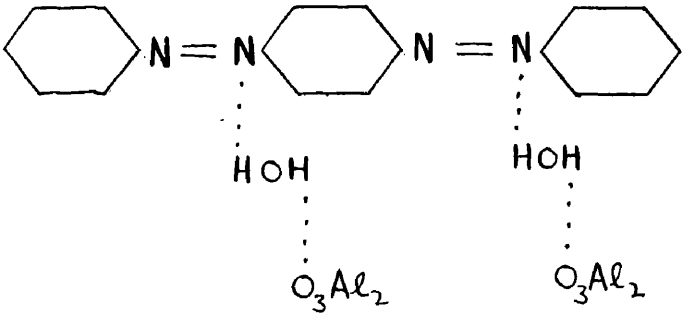
Adsorption experiments were carried out with solutions of azobenzene and bis(phenylazo)benzene in dry benzene, spectroscopic ethanol, absolute ethanol, and an ethanol-water mixture (80:20). Both compounds were adsorbed from aqueous ethanol but neither were adsorbed from the other solvents used.

This result indicates that the mechanism whereby unsubstituted azo-compounds are adsorbed on acidified alumina is similar to that operating in the case of the anodic film, viz. the water in the solvent acts as a hydrogen-bonding cross-linking agent forming bonds simultaneously with the oxygen of the alumina and one of the nitrogen atoms in the azo-linkage of the solute.

Isotherms illustrating the adsorption of azobenzene at 23° and 30°, and of bis(phenylazo)benzene at 30° are shown in Figs. 52 and 53. The fact that the adsorption of azobenzene decreases with rise in temperature shows that a measurable negative heat of adsorption is involved. This is further evidence that bonds are formed between the solute and the oxide.

The values of the affinities of azobenzene and bis(phenylazo)

benzene foralumina, calculated from the equation on p.55 on the assumption that adsorption takes place on specific sites in the substrate, are -3.6 kcal/mole and -4.2 kcal/mole respectively. The higher affinity value of the bisazo-compound suggests that both azo-linkages in the molecule are involved in its attachment to the oxide, i.e. there are two water "bridges" formed, as shown below.



These results having indicated that the formation of hydrogen bonds is a possible mode of attachment in the adsorption of compounds by alumina, experiments were carried out with substances containing other substituent groups capable of forming such bonds. The results are discussed below.

(i) Hydroxy-compounds.

The hydroxy-azo-compound, 2:4-dihydroxyazobenzene was found to be adsorbed from absolute ethanol (Table 11). This must clearly be attributable to the presence of the free hydroxy-group in the 4-position, as azobenzene is not adsorbed from this solvent.

Isotherms for the adsorption from water of phenol and resorcinol at 58° are shown in Fig.54. The affinities of these solutes, calculated from the isotherms are -2.4 kcal/mole and -3.2 kcal/mole for phenol and resorcinol respectively. The higher value for the dihydroxy-compound suggests that both the active groups may be attached to the surface of the substrate.

(ii) Amino-compounds.

The effect on adsorption behaviour of introducing amino-groups into otherwise unsubstituted azo-compounds was investigated by carrying out experiments with solutions of p-aminoazobenzene and phenylazo-2-naphthylamine in dioxan. Both compounds are adsorbed from this solvent at 58°, and the isotherms are shown in Fig.55. In the case of the phenylazo-compound, one of the hydrogen atoms of the amino-group is intramolecularly chelated, leaving only one capable of bonding this compound to the alumina. The value of its affinity for the substrate is -4.3 kcal/mole and that for p-aminoazobenzene is -5.4 kcal/mole. As found in the case of the hydroxy-compounds the affinity of a solute rises with the number of hydrogen atoms free to form external bonds.

The adsorption of amino-compounds on the anodic oxide film, which is a result of hydrogen-bond formation, is found to be prevented by using water or benzene as solvent. In order to discover if this is also the case with alumina solutions of the

compounds p-nitroaniline and m -nitroaniline in an ethanol-water mixture (50:50) were studied. Both compounds were adsorbed, as shown in Fig.56. In the case of the behaviour of Magenta P towards the anodic film (Fig.7), from solution in dioxan and two dioxan-water mixtures (75:25 and 50:50), only a very small amount was adsorbed from the solvent containing 50% water. The isotherms for the two nitroanilines studied show, however, very considerable adsorption of both compounds from aqueous ethanol and suggest that the presence of water does not prevent them being adsorbed.

(iii) Indications of adsorption by hydrogen-bonding through hydrogen attached to carbon.

A number of examples of intermolecular hydrogen-bonds involving hydrogen attached to carbon are known, e.g.[84], and an attempt was made to discover whether adsorption on alumina could take place by this means. Solutions of 2:4-diacetoxyazobenzene in dry benzene were used and adsorption was found to occur (Fig.57). As azobenzene is not adsorbed from the solvent employed here adsorption is presumably the result of hydrogen-bond formation thus:-

It is interesting to notice that no direct evidence of this type of bonding was found in the case of the anodic film. The results did, however, suggest that decomposition had occurred which in itself seems to show that some form of close association with the film took place.

An additional test to check that adsorption could occur by the formation of a hydrogen-bond between alumina and hydrogen attached to carbon, was made on the basis of work done by Arshid, Giles and Jain[79] on hydrogen-bond formation in solution. They found that glucose and cellobiose form hydrogen-bond complexes with reactive second solutes in water, apparently reacting in their open-chain form as aliphatic aldehydes. The normal equilibrium state of glucose in water is strongly in favour of the α- and β- ring structures, only a small percentage of the open-chain aldehyde being present. If, however, in the equilibrium mixture the aldehyde alone can form an intermolecular bond (the hydroxy- and ether groups probably being protected by solvation with water), then complex formation will alter the equilibrium in favour of the open-chain structure. Arshid et al. found that ketones do not form hydrogen-bond complexes in water, and neither do the ketoses, sucrose and fructose, so that in their case neither open-chain nor ring-bond can be reactive towards a second solute.

Accordingly the adsorption behaviour of sucrose and cellobiose towards alumina in aqueous solution was examined. Cellobiose was adsorbed, but sucrose was not. The isotherm for cellobiose is shown in Fig. 58. This result is thus quite in agreement with the conclusions of Arshid et al. and can be taken as evidence of hydrogen-bond formation between the hydrogen of the aldehyde group of cellobiose and alumina.

SECTION II.

The Adsorption of Sulphonated Azo-Compounds.

All the sulphonated azo dyes studied were found to be strongly adsorbed on acidified alumina from aqueous solution, the amount adsorbed at equilibrium being independent of temperature, (Figs. 59 to 68).

The fact that the dyes Orange II and 1-naphthylamine⟶R-acid are adsorbed is evidence that the presence of functional groups, other than sulphonate groups or azo-groups, is unnecessary for adsorption as the hydroxy-group in both these molecules is intramolecularly chelated and cannot take part in the formation of external bonds.

Attachment of these solutes to the substrate by the formation of a water bridge between a nitrogen atom of the azo-linkage and an oxygen atom at the alumina surface is unlikely, because a process of this type has been found to be accompanied by a measurable heat of adsorption (p.108).

The adsorption process would therefore appear to result either from the operation of van der Waals forces or reaction with the sulphonate groups in the solute molecule. Hesse and Sauter[106] studied the adsorption of neutral substances and of acid and basic dyes on alumina. They found that the adsorption

of neutral substances is unaffected by change in pH, whereas acid dyes are adsorbed more strongly as the pH decreases and basic dyes behave in the opposite manner. Cummings[121] has found that sulphonated azo dyes are not adsorbed by commercial chromatographic alumina, which gives a pH of ca. 9 in contact with water, but are adsorbed after the alumina has been treated with acid. Thus it appears that van der Waals attraction is not responsible for adsorption, which must clearly be attributed to the presence of sulphonate groups in the dye molecules.

Hesse and Sauter (loc.cit.) suggest that the dependence of the adsorption of acid and basic dyes on pH may show that a compound is formed between these dyes and the substrate. The absence of a measurable heat of adsorption observed in the present case does not, however, support this explanation of the process.

Wieland[103] has shown that alumina treated with hydrochloric acid takes up chloride ions and subsequently behaves as an anion exchanger. Many ion-exchange processes have been found to occur with negligible evolution of heat. The adsorption of cationic dyes from water by certain negatively charged surfaces (graphite, silica) has a negligible temperature coefficient[122] and several workers[123] have pointed out that temperature has little or no effect on base-exchange equilibria between ions of the same valency. Very low temperature coefficients have been observed also in cation-exchange on resins by Boyd et al. Magistad et al., Patton and

Ferguson and Vanselow[124]. Steinhardt, Fugitt and Harris[125] found a very low value for the heat of adsorption of monochloroacetic acid on wool at low temperatures (0.3 - 0.4 kcal/mole). They supposed that this was due to replacement of a solvated molecule of water in the fibre by another of the acid held only slightly more strongly.

It appears likely, therefore, that the adsorption of sulphonated azo dyes by acidified alumina is a purely physical process, involving chloride ion-dye anion exchange. The process is therefore different from the formation of bonds between the dye anion and aluminium which is found to occur when these solvents are adsorbed by the anodic oxide film.

(1) Adsorption Equilibria.

The nature of the isotherms.

The equilibrium adsorption isotherms for all the dyes studied conform to type I of the Brunauer et al.[86] classification (Fig.13). These isotherms have well-defined plateaux which, for the purposes of orientation measurements, may be taken as representing the existence of a monomolecular layer of adsorbed solute on the substrate.

Isotherms of this type were found by Boyd, Schubert and Adamson[126] in a study of cation-exchange on synthetic organic zeolites. On carrying out experiments at various solution:resin

weight ratios, however, they found that the amount adsorbed at equilibrium was not a function of the equilibrium bath concentration but depended on the ratio of the equilibrium concentrations in the solution and adsorbent phases. In view of this observation, the adsorption of Naphthalene Red J was studied at three solution: alumina weight ratios, viz. 25:1, 50:1 (the standard ratio), and 200:1. The results are plotted in Fig. 59 and it can be seen that the same isotherm is obtained regardless of the ratio used. This demonstrates that in the present case the equilibrium concentrations in the solution and adsorbent phases are inter-dependent. The process is thus a normal adsorption process.

Orientation of the adsorbed anions.

The surface area of the alumina available for the adsorption of sulphonated dye anions was estimated from the isotherm for Orange II (Fig.60). It was assumed that, when adsorbed, this compound is oriented normal to the surface of the alumina particles with the negatively charged sulphonate group adjacent to the adsorbent. The area occupied by the anion in this position was estimated from a Catalin (Stewart-type) scale molecular model as was done in the work on adsorption on the anodic oxide film. This area, multiplied by the monolayer capacity of the adsorbent for this anion which was estimated from the adsorption isotherms, gave a value of 5 $cm.^2/g. \times 10^{-5}$ for the specific surface area of the

alumina.

The area occupied by the other anions was then estimated by dividing the specific surface area of the alumina, as estimated above, by the monolayer capacity for each anion. In Table 12 these values are compared with the cross-sectional areas of the anions, measured from models, in the positions designated, "end-on", "edge-on" and "flat", on page 66. It will be seen from Table 12 that the areas of coverage of the anions calculated from isotherm data are in reasonable agreement with those measured from models if the anions are oriented in the monolayer according to the following general principles.

(i) The dye anions are attached to the substrate only through the sulphonate groups.

(ii) All the sulphonate groups are involved in the attachment.

(iii) Except in the case of the dyes having sulphonate groups disposed more or less symmetrically around the molecule, viz. sulphanilic acid ⟶ R-acid and Naphthalene Scarlet 4R, the anions are oriented at right angles to the surface. This is probably a result of the strong non-polar attraction between the hydrophobic residues of adjacent molecules.

(iv) The presence of an alkyl chain in the anion results in it covering a much smaller area than that covered by the non-alkylated anion. (Compare the results for the dyes Azogeranine,

Butylazogeranine and Dodecylazogeranine given in Table 12).

As in the case of orientation measurements on the anodic film, the value of the surface area of the substrate obtained in the above manner is derived on the assumption that completed close-packed monolayers are formed. The fact that the amount adsorbed at equilibrium is independent of temperature probably renders the value for the surface area obtained for the alumina powder more fundamental than that obtained for the anodic oxide film, which relates to adsorption at ca. 50° only.

Thermodynamic Data.

(i) The change in chemical potential.

As discussed in the general introduction (p.8) the mechanism of adsorption must be known before the basic equation for the determination of the change in standard chemical potential can be adapted to fit any given adsorption system. In the present case, the isotherms for all the sulphonated azo dyes examined conform to the shape fitted by Langmuir's adsorption equation. This assumes the existence of separate, independent, adsorption sites in the substrate and the formation of a monomolecular layer of solute on its surface. Evidence that a mechanism of this type is operative in the present instance, apart from the shape of the isotherm, is suggested by the comparatively consistent values of the surface area of the substrate obtained on the assumption that

a monolayer is formed and that the sulphonate groups are responsible for adsorption. Since anion-exchange is supposed to account for adsorption only the anions are adsorbed, the cations remaining in solution. On this basis, the equation used for the evaluation of the change in standard chemical potential is that given on p.69, for a dye Na_zD which is ionised in solution, viz.

$$-\Delta\mu^{o} = -RT \ln [Na]_s^z [D]_s$$

Where $[Na]_s^z [D]_s$ is the activity of the dye in solution at equilibrium. The values for $-\Delta\mu^{o}$, which give a quantitative measure of the affinities of the dyes for the substrate, are given in Table 13.

The values obtained can be explained on the basis of the hypothesis put forward in the case of adsorption on the anodic oxide film, viz., the total affinity of a dye is the sum of "partial" values for each of the sulphonate groups in the molecule, each of which contributes an amount dependent on its position in the molecule. For dyes based on the phenylazo- and naphthylazo-naphthalene skeletons it can be seen from Table 13 that this is in fact the case in the adsorption of sulphonated azo compounds by acidified alumina.

It appears also that only the sulphonate groups make significant contributions to the affinity as the dyes Congo Orange R

and Ponceau 6RB, which have two azo-linkages in the molecule, have affinity values similar to those of monoazo-compounds having sulphonate groups in similar positions in relation to the azo-linkages of the molecules.

The three dyes Azogeranine, Butylazogeranine, and Dodecyl-azogeranine have comparable affinities for the substrate, which indicates that alkyl chains have a negligible affinity for it.

(ii) The apparent entropy of adsorption.

The apparent entropy of adsorption for each dye at 50° was calculated from the equation.

$$\Delta\mu^{o} = \Delta H^{o} - T\Delta S^{o}$$

The values are given in Table 14.

It will be noted that these values are comparable to those obtained in the case of adsorption on the anodic film (less than -100 cal./mole/deg.) which suggests that there is a similar degree of order in the solute/adsorbent phases in both cases. The orientation measurements suggest that the adsorbed anions are rigidly oriented.

As there is no apparent heat of adsorption for any of the dyes studied, the values of the apparent entropy of adsorption, calculated using the above equation, are proportional to the affinities of the dyes

for the substrate. This introduces the possibility of calculating "partial entropies" for the sulphonate groups having values characteristic of their position in the molecule.

This may indicate that the positions of the sulphonate groups have an effect on the degree of order in the solute/adsorbent phase.

(2) Kinetics of Adsorption.

The results of preliminary rate-measurement experiments with 0.02% solutions of Naphthalene Red J showed that at temperatures greater than ca. 30° the system attained equilibrium in a few seconds. For this reason measurements were made at lower temperatures than 30°, within the range 9° to 25° in all cases. Even at these lower temperatures adsorption was found to be usually very rapid e.g., half the equilibrium amount of Naphthalene Red J adsorbed from a 0.02% solution at 25° is taken up in 5 seconds. To obtain reasonably accurate readings in the early stages of adsorption it was therefore necessary to modify the rate-measurement technique employed in the case of the anodic film where the attainment of equilibrium was a matter of hours at temperatures about 60°.

Tubes containing the test solutions were fitted with ground-glass stoppers and immersed in the thermostat at the appropriate temperature for some time to allow thermal equilibrium to be attained. One of the tubes was held in such a position in the

thermostat that the mouth was above the surface of the thermostat water. The stopper was removed and 0.1g. of acidified alumina quickly poured in, the stopper reinserted, and the agitating mechanism immediately started up. After the requisite time interval had elapsed, the agitation was stopped, the stopper removed, and a sample of the test solution quickly withdrawn for analysis. The tubes were dealt with singly to ensure that the time period measured from the moment all the alumina had been poured in until the sample for analysis had been withdrawn corresponded as closely as possible with the period of constant agitation of the system. It was found that reproducible readings could be obtained, by this procedure, for a 10 second immersion period.

Rate of adsorption isotherms were obtained at three temperatures for each of the dyes studied. Those for Naphthalene Red J at 25°, 14° and 9° are shown in Fig. 69. These curves are typical of those obtained for the other dyes studied and show that the rate of adsorption increases with temperature although the amount adsorbed is independent of temperature, as noted previously.

The form of the kinetics.

The results of the rate measurements were analysed in the light of the fact that the process of adsorption appears to be one of ion-exchange involving the Cl^{-} ions in the substrate and

the dye anions.

Ion-exchange adsorption does not involve the breaking of any covalent bonds and the rate of adsorption will therefore depend on the rate of transport of the anions in the bulk of the solution to the exchange sites in the adsorbent. This process may be broadly divided into two stages, viz.,

(i) Diffusion of anions through the solution to the surface of the adsorbent particle.
(ii) Diffusion of anions inside the adsorbent particle from the outer surfaces.

The experimental technique employed to measure the rate of adsorption ensured vigorous agitation of the adsorption system. This would be expected to minimise the effect of (i) so that, at least in the early stages of the process, it would be reasonable to assume that a layer of solution of constant concentration of the solute exists at the adsorbent particle-solution interface. In this case it is likely that the rate-controlling process would be (ii). On the other hand, the uptake of anions was found to be very rapid and the transport of anions from the bulk of the solution after the first stages of the adsorption might not occur with sufficient speed to maintain a layer of constant solute concentration at the absorbent surface. In this case the adsorbent particles may be considered to be enveloped in a liquid film

in which a concentration gradient persists. Thus it is evident that both (i) and (ii) must be taken into account in the present case and the development of equations which are applicable to the two diffusion processes is described briefly below.

(i) Diffusion through the bonnding liquid film.

The Nernst static diffusion theory is likely to be only a crude approximation for the complex situation which exists near an irregular solid surface in a stirred liquid, nevertheless, Boyd, Adamson and Myers[127] have found that under a given set of conditions of temperature and stirring its application is useful for the treatment of exchange kinetics. Kressman and Kitchener[128] have applied the theory to diffusion from a limited bath in the case of cation-exchange on a phenolsulphonate resin. In the present case, an equation describing this type of diffusion may be derived as follows.

Let Q_o be the number of milli-equivalents of Cl^- ion in the alumina which is brought into contact with V ml. of solution containing Q_o milli-equivalents of the salt of dye anion D^- at time $\underline{t} = 0$. Suppose that the adsorbent consists of $\underline{n}$ particles of alumina of mean equivalent sphere radius $\underline{r}$, and that the effective thickness of the Nernst diffusion layer is $\underline{\delta}$. Let the amount of exchange after time $\underline{t}$ be Q_t milli-equivalents. The diffusion process taking place in the Nernst layer is essentially one of

anion exchange at constant ionic strength and the rate is therefore proportional to the concentration gradient of Cl^- or D^-. Let D_1 be the Fick's law diffusion coefficient for the inter-diffusion of the anions under these conditions.

After time t, the concentration of Cl^- ions on the solution side of the Nernst layer will be Q_t/V. A satisfactory expression for the concentration of Cl^- ions at the adsorbent surface is, more difficult to obtain. It is likely however, that the number of anions present at the outer surface of the particles derived from the adsorbent phase is much greater than that present as soluble electrolyte from the solution phase since soluble cations are to a great extent repelled by the opposing zeta potential[129]. Consequently, the number of Cl^- ions which can participate in diffusion away from the surface of the particle at any instant may be taken as proportional to the number present in the adsorbent. This number may be written $k'(Q_o - Q_t)$.

Application of Fick's law to the Nernst layer, assuming the diffusion gradient to be linear, gives,

$$\frac{dQ_t}{dt} = \frac{D_1}{\delta} \left\{ k'(Q_o - Q_t) - \frac{Q_t}{V} \right\}$$

which on integrating gives,

$$\frac{Q}{Q_o} \ln\left\{1 - \frac{Q_t}{Q}\right\} = kt \qquad \ldots\ldots\ldots (1)$$

where Q_∞ = amount of Cl^- ion which has passed into the solution when the system is at equilibrium, and $\underline{k} = D_1 k'/\delta$, which is a constant.

Thus, if the rate of adsorption is controlled by diffusion through the bounding liquid film, the plot of $-\log((1 - Q_t/Q_\infty)$ against $\underline{t}$ should give a stright line, whose gradient is proportional to the diffusion coefficient in the film.

(ii) Diffusion inside the adsorbent particle.

Boyd, Adamson and Myers[127] have shown that the kinetics of an ion-exchange process are formally similar to those for the conduction of heat into a sphere from a well-stirred, infinite bath, assuming that the concentration in the solution is uniform up to the particle surface and that the rate of exchange is controlled by radial diffusion inwards from the particle surface with a constant diffusion coefficient. The corresponding theory for a limited bath has been given by Carslaw and Jaeger[130] and in a more convenient form by Paterson[131]. It has been shown by Barrer[132] that Paterson's solution approximates to the following expression for small values of Q_t/Q_∞,

$$\frac{Q_t}{Q_\infty} = \frac{6}{r}\frac{Q_o}{(Q_o - Q_\infty)}\sqrt{\frac{Dt}{\pi}} \quad \ldots\ldots\ldots \quad (2)$$

Thus a straight line should be obtained for a plot of Q_t/Q_∞ against $\sqrt{t}$ if particle diffusion is the rate-controlling process in exchange adsorption. Kressman and Kitchener[128] have found this rule to be obeyed up to $Q_t/Q_\infty = 0.8$ in some cases, but in general it can only be expected to hold for smaller values of Q_t/Q_∞.

Determination of the rate-controlling process.

By plotting the experimental results for each dye at each temperature in accordance with both equations (1) and (2), the diffusion process controlling the rate of adsorption was determined. Figs. 70 and 71 show the results for Naphthalene Red J (0.02%) at 25°, 14° and 9° plotted in accordance with equations (1) and (2) respectively. It is clear from these figures that the kinetics at 25° and 14° are best described by equation (1) whereas at 9° they fit equation (2). Thus the rate of adsorption is controlled by particle diffusion at 9° and by diffusion in the bounding film and the higher temperatures. This is quite logical when the conditions necessary for the two processes are considered. At 25° the uptake of anions is exceedingly rapid and the maintenance of a layer of constant solute concentration at the adsorbent particle surface may not be possible. At 9°

the rate of adsorption is very much slower, the time required for half the equilibrium amount to be adsorbed being 85 seconds against 5 seconds at 25°, and in the vigorously agitated systems it is likely that adsorption takes place from a bath of virtually constant solute concentration, the rate of adsorption being controlled by diffusion inwards from the surface of the adsorbent particles. This is found to be the case up to $Q_t/Q_\infty = 0.7$.

The results for the other dyes studied, plotted in the appropriate manner, are shown in Figs. 72 to 76. In certain cases, where the plot is made on the film diffusion basis, it will be seen that in the early stages of adsorption the points do not lie on the line. This is possibly because, over the first few seconds of adsorption, conditions for particle diffusion are fulfilled and the rate of adsorption is thus, over this period, controlled by this process.

It may thus be concluded that while only one case, that of the adsorption of Naphthalene Red J at 9°, is fitted well by the particle diffusion equation, it is likely that the early stage of adsorption is rate-controlled by this process. As the system approaches equilibrium, however, the rate is controlled by diffusion through a bounding liquid film. In some cases the rate of adsorption is controlled throughout by film diffusion, but from the experimental evidence obtained it is not possible to relate dye anion structure to its dependence on either mechanism.

Activation energy of diffusion.

Determination of the activation energy of diffusion might be expected to provide further information about the adsorption mechanism.

For activated diffusion processes, the diffusion coefficient varies with the temperature according to the equation,

$$D_T = D_o \cdot e^{\left(\frac{-E}{RT}\right)}$$

where D_o = a constant and E = the activation energy.

The activation energy is determined by measuring the slope of the line obtained by plotting the values of D_T against the reciprocal of the absolute temperature. The lines thus obtained for the dyes studied are shown in Fig. 77 and the values of the activation energies determined from these lines are shown in Table 15.

The activation energies for the diffusion of the dyes Naphthalene Red J, Naphthalene Red EA and 1-naphthylamine → R-acid can be seen from Table 15 to be 9.2, 12.5 and 13.0 kcal./mole respectively. The observed kinetics of adsorption of these dyes are best fitted by assuming that the rate-controlling process is one of diffusion through a liquid film surrounding the particles of the substrate, viz. Figs. 70, 71, 72 and 73. The value of the activation energy required for such a process

might reasonably be expected to be comparable to that required for diffusion in solution, which does not seem to be the case for these three dyes.

The low activation energies found for the dyes sulphanilic acid ⟶ R-acid, Poncean 6RB and Congo Orange R (Table 15) do, however, support the evidence of Figs. 74, 75 and 76, which indicate that the rate-controlling process in the adsorption of these dyes is one of diffusion through a bounding liquid film.

Considering the activation energy values given in Table 15, it may be significant that the three monoazo dyes having molecules based on the naphthylazonaphthalene nucleus have comparatively high values (ca. 10 kcal./mole), while those corresponding to the diffusion of disazo dyes are very much lower (ca. 3.5 kcal./mole).

Thus molecular structure of a dye may correlate with its activation energy of diffusion as was suggested by the work on the adsorption of sulphonated azo dyes by the anodic film (see p.92).

The very low activation energy found for diffusion of the dye sulphanilic acid ⟶ R-acid (1.4 kcal./mole) may also be related to its molecular structure, but as no other dye having a similar basic structure was studied it cannot be concluded that the adsorption of such dyes is characterised by very low activation energies.

CONCLUSIONS.

The conclusions drawn from the results of the investigation into the adsorption of organic solutes by alumina powder acidified by treatment with hydrochloric acid, and which have already been given in the text are, for convenience, summarised below.

The adsorption of solutes from dry organic solutes appears to occur only when the solute molecule contains at least one hydrogen atom free to form an intermolecular bond. Thus 2:4-dihydroxyazobenzene, p-aminoazobenzene, and phenylazo-2-naphthylamine are adsorbed from dry solvents whereas azobenzene and bis(phenylazo)benzene are not. These results indicate that the formation of hydrogen-bonds plays an important part in adsorption.

It was found that the affinity for the substrate of a compound capable of forming two intermolecular hydrogen-bonds was higher than that of a compound capable of forming only one, For instance,the affinity values determined for p-aminoaxobenzene and phenylazo-2-naphthylamine, both in dioxan solution, are -5.4 kcal./mole and -4.5 kcal./mole respectively, and those determined for resorcinol and phenol, both in aqueous solution, are -3.2 kcal./mole and -2.4 kcal./mole respectively.

The presence of water was not found to interfere with the adsorption of amino-compounds as was the case with adsorption on the anodic oxide film (see p.53).

The adsorption of unsubstituted azo-compounds which does not occur from dry solvents, was found to be promoted by the presence of water. This appears to be due to the formation of a water "bridge" between the solute and the substrate involving the simultaneous formation of bonds by the hydrogen atoms in the water molecule.

The affinity of bis(phenylazo)benzene (-4.2 kcal./mole) for the substrate is higher than that of azobenzene (-3.6 kcal./mole) which suggests that in the case of the former solute two water "bridges" are formed in adsorption, while only one is formed in the case of the latter.

There is evidence that compounds can be adsorbed by the formation of hydrogen-bonds with hydrogen attached to carbon. 2:4-diacetoxyazobenzene was found to be adsorbed from dry benzene, whereas azobenzene is not adsorbed from this solvent.

The results of experiments carried out with aqueous solutions of sucrose and cellobiose show that only the latter solute is adsorbed. Arshid et al.[79] found that cellobiose can form hydrogen-bond complexes with reactive

second solutes in water, apparently reacting in the open-chain form as an aliphatic aldehyde. Sucrose, however, was found to be incapable of forming hydrogen-bond complexes in water. Hence the adsorption of cellobiose and non-adsorption of sucrose by acidified alumina powder seems to underline the importance of hydrogen-bond formation in adsorption by this substrate as well as showing that hydrogen attached to carbon is effective in promoting adsorption.

Sulphonated azo dyes were found to be strongly adsorbed from aqueous solution, the amount adsorbed at equilibrium being independent of temperature. The absence of a measureable heat of adsorption suggests that the adsorption mechanism does not involve a chemical reaction. It has been found (121), however, that these dyes are not adsorbed on alkaline alumina which rules out van der Waals attraction as an adsorption mechanism.

The most likely mechanism seems to be one of ion exchange between the dye anions and the chloride ions taken up during preparation of the substrate by washing with hydrochloric acid.

Consideration of isotherm data suggests that the dye anions are adsorbed in a monolayer. Orientation measurements indicate that the anions are attached to the substrate only

through their sulphonate groups and that all the sulphonate groups are involved in the attachment.

The affinity of the dyes for the film appears to be the sum of the affinities of the sulphonate groups in the molecule, each contributing to the total affinity an amount characteristic of its position in the molecule. Only the sulphonate groups make significant contributions to the affinity of the anion.

The values of the apparent entropy of adsorption determined are similar to those obtained in adsorption on the anodic film (less than-100 cal./mole/deg.).

Although the entropy change is not very large orientation measurements suggest that there is a high degree of order in the monolayer.

A study of the kinetics of adsorption of sulphonated azo dyes shows that the rate-controlling process, except in the earliest stages, is in most cases one of diffusion of anions through a layer of solution surrounding the particles of the substrate. The rate of adsorption of the dye Naphthalene Red J was, however, found to be controlled by diffusion inside the particles of the substrate at 9° and by diffusion through the bounding liquid film at higher temperatures ($14^{\circ}$and 25°). This may be explained by the fact that at the higher temperatures the uptake of anions is very rapid and the maintenance of a layer of constant

solute concentration at the surface of the adsorbant particles is unlikely.

In all cases studied the results suggest that in the earliest stages of adsorption the rate is controlled by diffusion in the particles of the substrate.

The activation energies of diffusion were determined for several dyes. There does not appear to be a correlation between activation energy and the form of the kinetics but the values determined seem to be to some extent dependent on the structure of the dye anions.

COMPARISON OF THE ADSORPTION BEHAVIOUR OF THE TWO SUBSTRATES.

The results of the present work bring to light some striking differences in the adsorption behaviour of the two substrates studied.

The following types of adsorption mechanism are found to operate in the adsorption of organic solutes from solution on one or both substrates.

(i) Hydrogen-bond formation with phenols and amines.

(ii) Hydrogen-bond formation involving hydrogen attached to carbon in the solute molecule.

(iii) "Bridge-bonding" through water whereby unsubstituted azo-compounds are adsorbed in presence of water.

(iv) Chelation between the aluminium of the substrate and suitable pairs of ortho-substituents in the solute molecule.

(v) Salt formation between the aluminium of the substrate and sulphonated azo compounds.

(vi) Ion-exchange between sulphonated anions and chloride ions in the substrate.

Found to operate in adsorption by the anodic oxide film

Found to operate in adsorption by acidified alumina powder

Found to operate in adsorption by both substrates

Mechanism (iv) was not studied in the case of acidified alumina powder.

Mechanism (ii).

It has been noted previously (p.58) that the results of experiments carried out with 2:4-dihydroxyazobenzene and the anodic oxide film were inconclusive owing to suspected decomposition of the solute.

This compound was, however, adsorbed on acidified alumina powder.

It should be noted that this difference in the action of the two substrates is possibly accounted for by the fact that the test solutions were in contact with the anodic oxide film for 36 hours at 60° and 48 hours at 33°, whereas, in the experiment with alumina powder, the contact time was only 30 minutes at 44°.

Thus, in the case of the anodic film, the very much longer contact time would enhance any catalytic decomposing action of the substrate.

Considering that some form of close association between solute and substrate must have occurred for decomposition to take place, mechanism (ii) may, in fact, operate in adsorption by both substrates.

The kinetics of adsorption.

The differences in the kinetic aspect of adsorption by

the two substrates may be summarised as follows:

(i) Rate of adsorption.

The rate of adsorption of the sulphonated azo dyes studied is very much slower in the case of the anodic oxide film.

(ii) The form of the kinetics.

The rate-controlling step in the adsorption of sulphonated azo dyes by the anodic oxide film is diffusion in the pores of the film, whereas in the case of the alumina powder the rate is controlled by diffusion through the bounding liquid film.

The differing forms of the kinetics for the two substrates is not surprising if their physical structures are taken into account.

The powder substrate has a very much higher external surface area:weight ratio. Most of the equilibrium amount of solute will be adsorbed, more or less, externally. The equilibrium amounts of solutes adsorbed by the anodic oxide film, on the other hand, indicate that the greater part is adsorbed inside the pores and the solute molecules or anions must therefore pass along pores whose diameters are of molecular dimensions.

This also explains the much greater speed of adsorption by the powder substrate.

PRACTICAL ASPECTS OF THE WORK.

The aim in the present work has been to determine the nature of the forces operating in the adsorption of organic solutes by two forms of alumina, one commercially important, and the other of importance to the chemist.

It is hoped that, by providing information as to the parts played by various functional groups; azo-, hydroxy-, amino-, acetoxy-, sulphonate and etc., in adsorption, the results of this work will be of practical use in two ways.

First, in the formulation of sulphonated azo dyes for dyeing anodised aluminium. The effect of the degree of sulphonation and the position of the sulphonate groups on the affinity of a dye for the substrate should be of use in this instance. Work on the light fastness of anodic films dyed with sulphonated azo dyes would of course by necessary.

Second, in the case of chromatographic alumina it is hoped that the results of the static adsorption experiments carried out will be of help in predicting the behaviour of some compounds, particularly of sulphonated azo dyes when flowing down alumina columns. Work on this subject is, in fact, being carried out by the Author.

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TABLE 1.

Azobenzene

Solvent	Temp. (°C)	Initial Concn. (g./l.)	Optical Density Readings.	
			Initial.	Final.
Dry benzene	40.0	0.20	1.110	1.112
		0.12	0.682	0.682
		0.04	0.233	0.232
Absolute ethanol	40.0	0.20	1.110	1.112
		0.12	0.682	0.685
		0.04	0.233	0.236
Ethanol-water (80-20)	40.7	0.20	1.110	1.030
		0.12	0.682	0.615
		0.08	0.436	0.400
		0.04	0.233	0.207

TABLE 2.

2:4-Dihydroxyazobenzene

Solvent	Temp. (°C)	Initial Concn. (g./l.)	Optical Density Readings.	
			Initial.	Final.
Absolute ethanol	33.1	0.20	0.092	0.083
		0.16	0.077	0.057
		0.08	0.067	0.018
	59.8	0.20	0.093	0.088
		0.16	0.077	0.066
		0.08	0.067	0.019

TABLE 3.

Orientation Data for Sulphonated Azo Dye Anions Adsorbed on the Anodic Film.

Compound	Temp. (°C)	Cross-sectional area of anion (A^2)			Max. adsorption (mmole/kg.)	Experimental area of coverage of anion. (A^2)
		End-on	Edge-on	Flat		
Monosulphonates.						
Orange II	50	50	80	150	400	50
Orange I	50	50	80	150	350	57
Naphthalene Red J	50	50	80	170	350	57
Disulphonates.						
Azogeranine	50	60	95	190	200	100
Dodecylazo-geranine	50	60	95	250	250	80
Aniline → R-acid	52	65	80	200	180	110
Dodecylaniline → R-acid	50	65	80	250	215	95
1-Naphthylamine → R-acid	50	65	80	190	70	280
Sulphanilic acid → 2-naphthol-6-sulphonate	50	65	85	160	100	200
Naphthalene Red EA	50	65	85	250	125	133
Trisulphonates.						
Sulphanilic acid → R-acid	50	65	85	225	65	308
Naphthalene Scarlet 4R	50	65	85	220	65	308
Tetrasulphonate.						
Sky Blue FF	50	65	130	380	65	308

TABLE 4.

Thermodynamic Data for the Adsorption of Sulphonated Azo Dyes by the Anodic Film.

Compound	Temp. (°C)	Affinity ($-\Delta\mu$) (kcal./mole)	Heat of Adsorption ($-\Delta H$) (kcal./mole)	Entropy of Adsorption ($-\Delta S$) (cal./mole/deg.)
Monosulphonates.				
Orange II	50	9.7	8.0	5.3
	59			
Orange I	50	8.8		
Naphthalene Red J	50	8.8	7.5	4.0
	59			
Disulphonates.				
Azogeranine	50	12.6	8.5	12.7
	60			
Dodecylazo-geranine	50	17.7	7.0	+33.0
	60			
Aniline→R-acid	40			
	52	17.7	7.5	31.0
Dodecylaniline → R-acid	50	18.6	32.0	43.0
	60			
1-Naphthyl-amine→R-acid	50	16.0		
Sulphanilic acid→2-naphth-ol-6-sulphonate	50	13.1		
Naphthalene Red EA	50	13.4		
Trisulphonates.				
Sulphanilic acid→R-acid	50	26.2	11.5	45.0
Naphthalene Scarlet 4R	50	18.8		

TABLE 4.

(contd.)

Compound	Temp. (°C)	Affinity ($-\Delta\mu$) (kcal./ mole)	Heat of Adsorption ($-\Delta H$) (kcal./mole)	Entropy of Adsorption ($-\Delta S$) (cal./mole/ deg.)
Tetrasulphonate.				
Sky Blue FF	50 60	28.6	12.0	51.0

TABLE 5.

Analysis of Affinities of Sulphonated Azo Dyes for the Anodic Film.

Compound	Position of sulphonate groups.	Measured Affinity ($-\Delta\mu$) (kcal./mole)	Partial Affinity ($-\delta\mu$) (kcal./mole)
Orange I	4	8.8	for sulphonate grp. in 4-posn. = 9.0 (approx.)
Orange II	4	9.7	
Naphthalene Red J	4	8.8	
Naphthalene Red EA	4, 6	13.4	hence for sulphonate grp. in 6-posn. = 4.5 (approx.)
Sulphanilic acid→2-naphthol-6-sulphonate	4, 6	13.1	$-\Delta\mu$ as predicted from above $-\delta\mu$'s = 13.5 (approx.)
Aniline→R-acid	3, 6	17.7	for sulphonate grp. in 3-posn. = 13.2 (approx.)
Sulphanilic acid→R-acid	4, 3, 6	26.2	$-\Delta\mu$ as predicted from above $-\delta\mu$'s = 26.7 (approx.)
Naphthalene Scarlet 4R	4, 6, 8	18.8	hence for sulphonate grp. in 8-posn. = 5.3 (approx.)

TABLE 6.

Variation of Specific Surface Area of the Anodic Film with Solution:film weight Ratio.

Compound	Area of coverage of anion (A^2)	Solution: film wgt. ratio	Max.adsorption (mmole/kg.)	Surface Area of film ($cm^2/kg. \times 10^8$)
Orange I (Max.adsorption from B.E.T. eqn.)	50	2500:1	700	35.00
		1250:1	410	20.50
		133:1	120	6.00
Orange II	50	833:1	390	19.50
		300:1	175	8.75
		133:1	90	4.50
1-Naphthylamine → R-acid	80	1666:1	370	28.80
		833:1	270	21.40
		133:1	60	4.8
Sulphanilic acid → R-acid	225	1666:1	130	29.25
		833:1	90	20.25
		133:1	22	4.95

Temperature = 59° in all cases.

TABLE 7.

Solubility of the Anodic Film in Water.

Solution:film wgt. ratio	Average % of original film dissolved.
1400:1	2.185
300:1	0.810
150:1	0.490

TABLE 8.

Co-ordinates of the Apparent Origins of Fick's Law Plots for Sulphonates Azo Dyes.

Compound	x-co-ordinate (mmole/l.)	y-co-ordinate (mmole/kg.)
Orange I	1.2.	9.0
Methylated Orange I	1.0	10.0
Orange II	2.6	17.0
Naphthalene Red J	2.2	40.0
Naphthalene Red EA	1.7	13.0
Naphthalene Scarlet 4R	1.1	1.5
Aniline → R-acid	1.8	-2.5
Butylaniline → R-acid	1.8	3.0
Dodecylaniline → R-acid	0.4	5.0
Azogeranine	1.8	5.0
Butylazogeranine	2.6	14.0
Dodecylazogeranine	4.9	43.0
Aniline → H-acid	0.6	-9.0
Butylaniline → H-acid	1.6	-2.0

TABLE 9.

Activation Energies for Diffusion of Sulphonated Azo Dyes in the Anodic Film.

Compound	Activation Energy (- E_A) (kcal/mole)
Monosulphonates.	
Orange II	8.8
Orange I	13.9
Methylated Orange I	10.3
Naphthalene Red J	4.2
Disulphonates.	
Azogeranine	10.8
Butylazogeranine	27.7
Dodecylazogeranine	6.7
Aniline ⟶ H-acid	10.5
Butylaniline ⟶ H-acid	13.8
Aniline ⟶ R-acid	16.2
Butylaniline ⟶ R-acid	16.3
Dodecylaniline ⟶ R-acid	11.9
Naphthalene Red EA	12.8
Trisulphonate.	
Naphthalene Scarlet 4R	6.2

TABLE 10.

Activation Energies for Diffusion of Sulphonated Azo Dyes in Aqueous Solution.

Compound	Activation Energy - E_A (kcal/mole)
Azogeranine	4.4
Butylazogeranine	4.2
Dodecylazogeranine	3.8

TABLE 11.

Adsorption of 2:4-Dihydroxyazobenzene on Acidified Alumina.

Solvent	Temp. (°C)	Initial Concn. (g./l.)	Optical Density Readings.	
			Initial.	Final.
Absolute ethanol	58.0	1.0 0.8 0.4 0.2	0.670 0.530 0.283 0.152	0.608 0.502 0.253 0.132

TABLE 12.

Orientation Data for Sulphonated Azo Dye Anions Adsorbed on Acidified Alumina.

Compound	Temp. (°C)	Cross-sectional area of anion (A^2)			Max. adsorption (mmole/kg.)	Experimental area of coverage of anion. (A^2)
		End-on	Edge-on	Flat		
Monosulphonates.	VALUES INDEPENDENT OF TEMPERATURE					
Orange II		50	80	150	166	50
Naphthalene Red J		50	80	170	175	48
Disulphonates.						
Azogeranine		60	95	190	80	104
Butylazo-geranine		60	95	220	132	63
Dodecylazo-geranine		60	95	250	124	67
Ponceau 6RB		65	110	200	62	134
Congo Orange R		65	140	375	106	79
Naphthalene Red EA		65	85	250	100	83
1-Naphthyl-amine → R-acid		65	80	190	104	80
Trisulphonates.						
Sulphanilic acid → R-acid		65	85	225	58	143
Naphthalene Scarlet 4R		65	85	220	68	122

TABLE 13.

Analysis of Affinities of Sulphonated Azo Dyes for Acidified Alumina.

Compound	Position of sulphonate groups.	Measured Affinity ($-\Delta\mu$) (kcal/mole)	Partial Affinity ($-\delta\mu$) (kcal/mole)
Monoazo Dyes.			
Orange II Naphthalene Red J	4′, 4′	11.9 12.6	for sulphonate grp. in 4-posn. = 12.0 (approx.)
Naphthalene Red EA	4′, 6	19.1	hence for sulphonate grp. in 6-posn. = 7.0 (approx.)
1-Naphthylamine ⟶ R-acid	3, 6	20.8	hence for sulphonate grp. in 3-posn. = 14.0 (approx.)
Sulphanilic acid ⟶ R-acid	4′, 3, 6	31.3	$-\Delta\mu$ as predicted from above $-\delta\mu$'s = 33.0 (approx.)
Naphthalene Scarlet 4R	4′, 6, 8	27.7	hence for sulphonate grp. in 8-posn. = 9.0 (approx.)
Azogeranine Butylazogeranine Dodecylazogeranine		19.0 17.9 18.2	

TABLE 13.

(contd.)

Compound	Position of sulphonate groups.	Measured Affinity ($-\Delta\mu$) (kcal/mole)	Partial Affinity ($-\delta\mu$) (kcal/mole)
Disazo Dyes.			
Ponceau 6 RB	4', 8	19.8	$-\Delta\mu$ as predicted from above $-\delta\mu$'s = 21.0 (approx.)
Congo Orange R	3, 6	19.4	$-\Delta\mu$ as predicted from above $-\delta\mu$'s = 21.0 (approx.)

TABLE 14.

Apparent Entropy of Adsorption of Sulphonated Azo Dyes on Acidified Alumina.

Compound	Temperature (°C)	Apparent Entropy of Adsorption ($-\Delta S$) (cal/mole)
Monosulphonates.		
Orange II	50	37.0
Naphthalene Red J	"	39.0
Disulphonates.		
Naphthalene Red EA	"	59.0
1-Naphthylamine ⟶ R-acid	"	65.0
Azogeranine	"	59.0
Butylazogeranine	"	56.0
Dodecylazogeranine	"	57.0
Ponceau 6RB	"	61.0
Congo Orange R	"	60.0
Trisulphonates.		
Naphthalene Scarlet 4R	"	86.0
Sulphanilic acid ⟶ R-acid	"	97.0

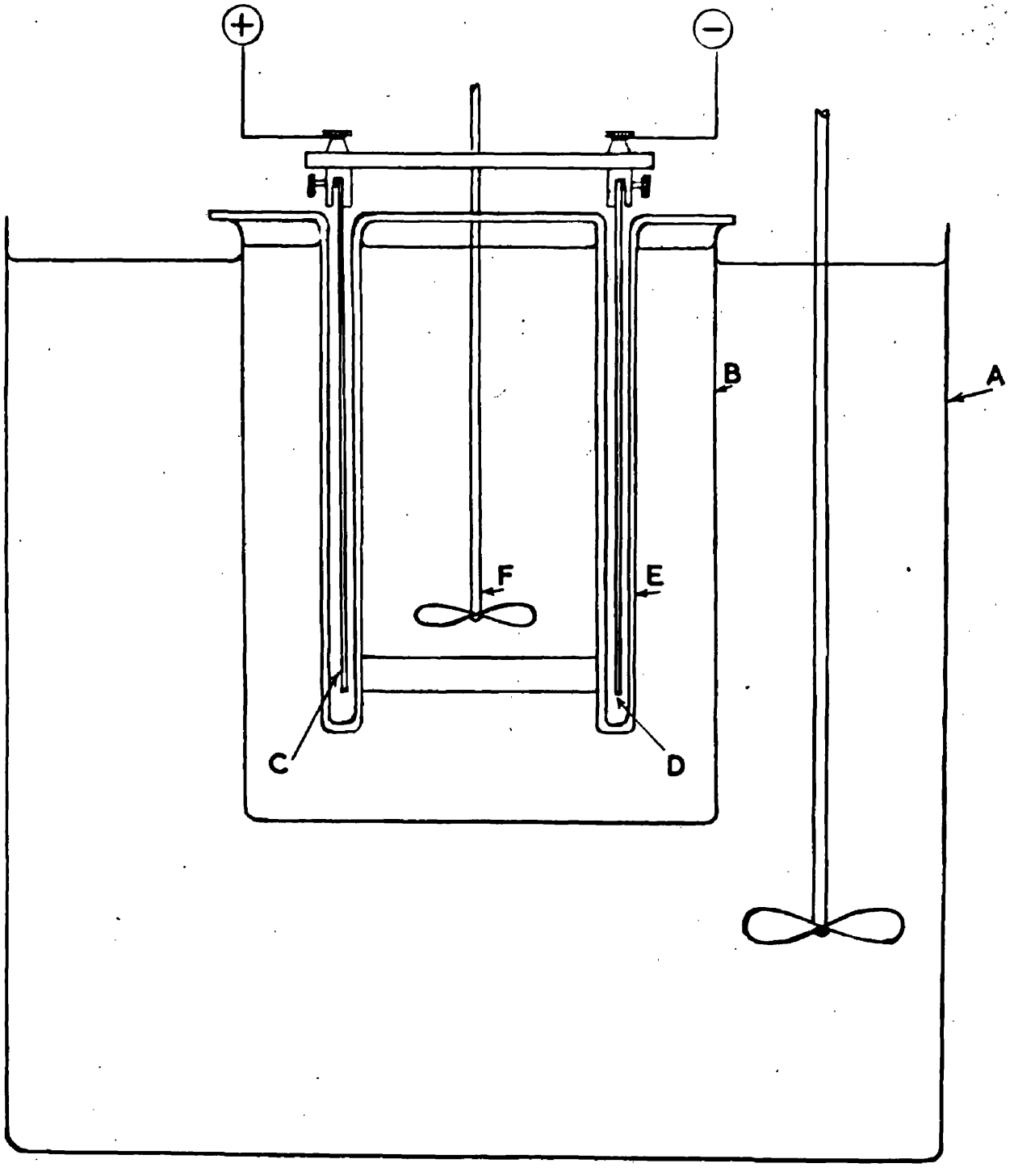
TABLE 15.

Activation Energies for Adsorption of Sulphonated Azo Dyes in Acidified Alumina.

Compound	Activation Energy ($-E_A$) (kcal./mole)
Naphthalene Red J	9.2
Naphthalene Red EA	12.5
1-Naphthylamine ⟶ R-acid	13.0
Sulphanilic acid ⟶ R-acid	1.4
Ponceau 6RB	3.9
Congo Orange R	3.2

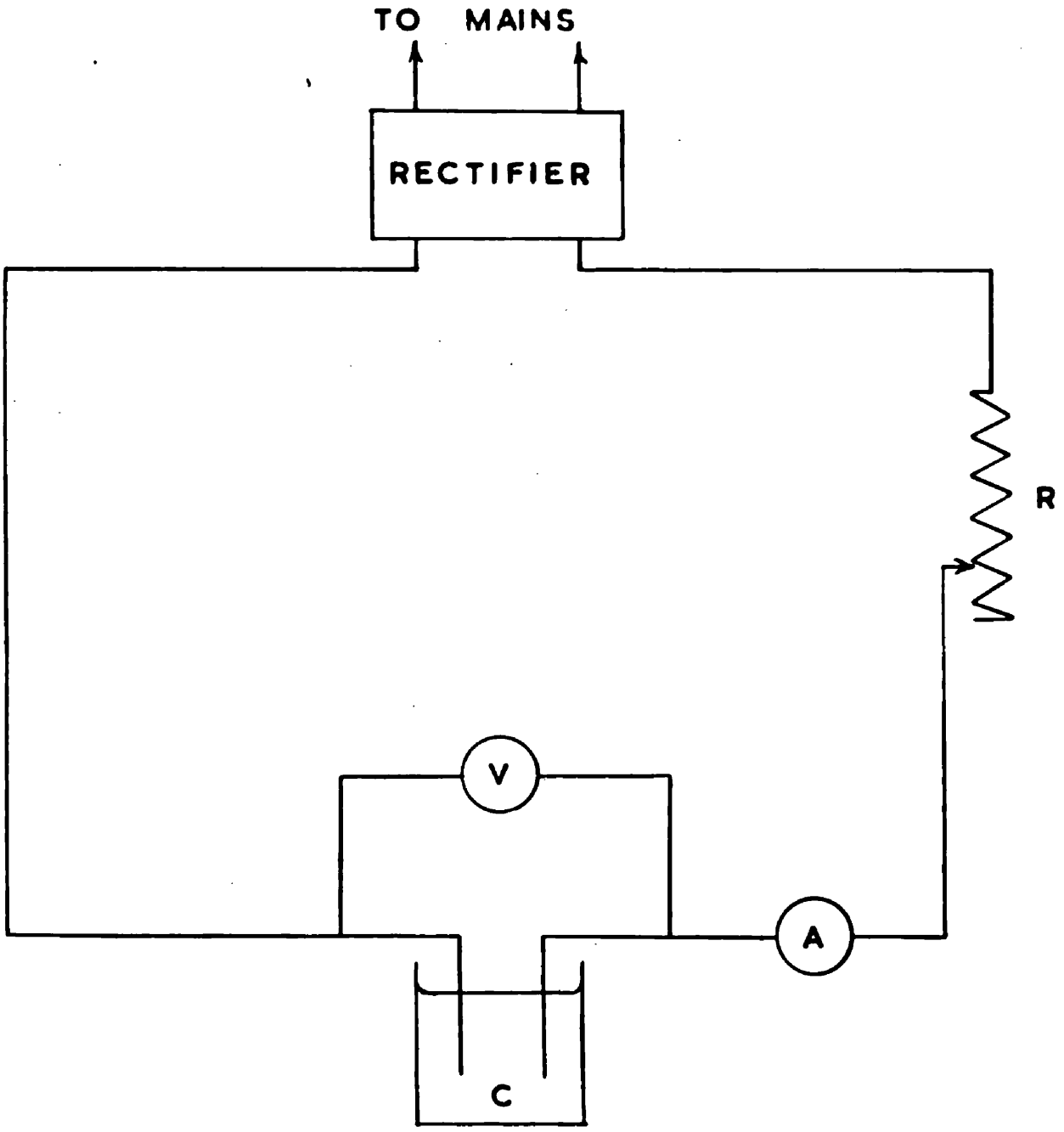
ADSORPTION ON ANODISED ALUMINIUM.

FIG. 1 ANODISING APPARATUS



A. THERMOSTAT TANK.
B. ANODISING CELL.
C. ALUMINIUM ANODE.
D. LEAD CATHODE.
E. PERSPEX FRAME.
F. SLOW SPEED STIRRER.

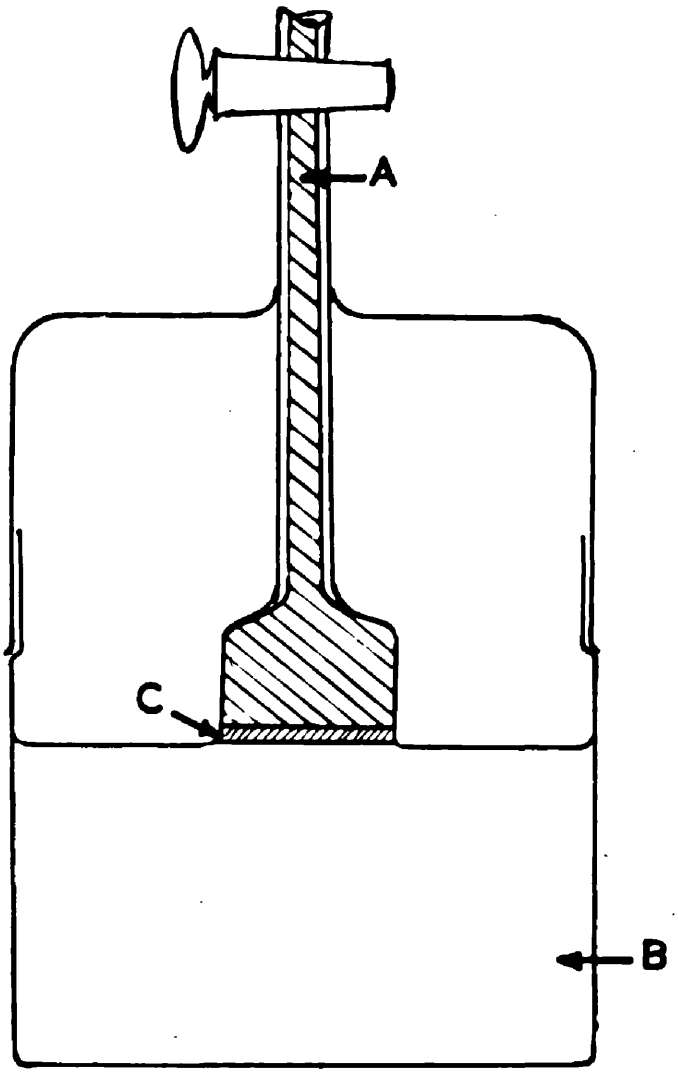
FIG. 2 ANODISING CIRCUIT



A = AMMETETER ; V = VOLTMETER ; C = CELL ;

R = VARIABLE RESISTANCE.

FIG. 3 DIFFUSION CELL

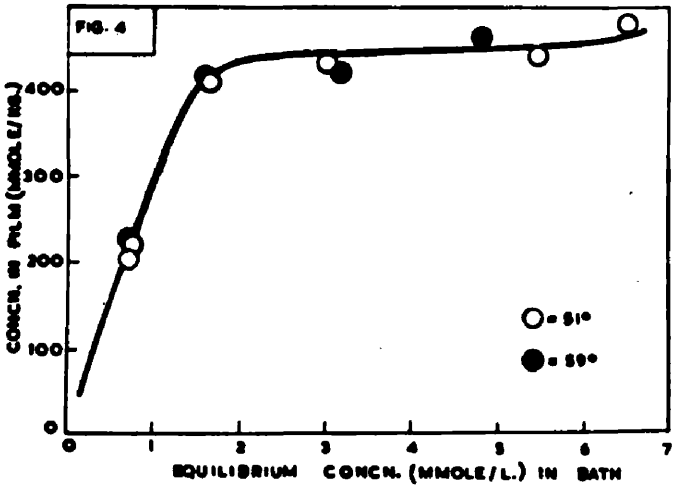


A. = DYE SOLN. IN INNER COMPARTMENT.

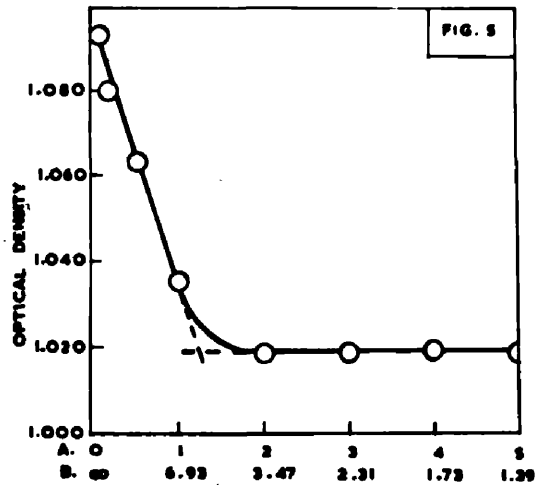
B. = DISTILLED WATER IN OUTER COMPARTMENT.

C. = SINTERED GLASS DISC.

ADSORPTION OF ALIZARIN



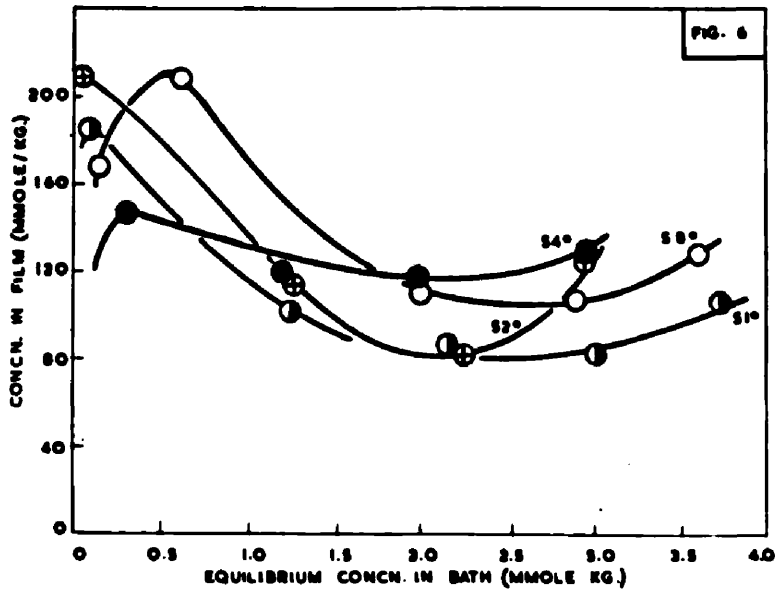
ALIZARIN — ALUMINIUM SULPHATE TITRATION



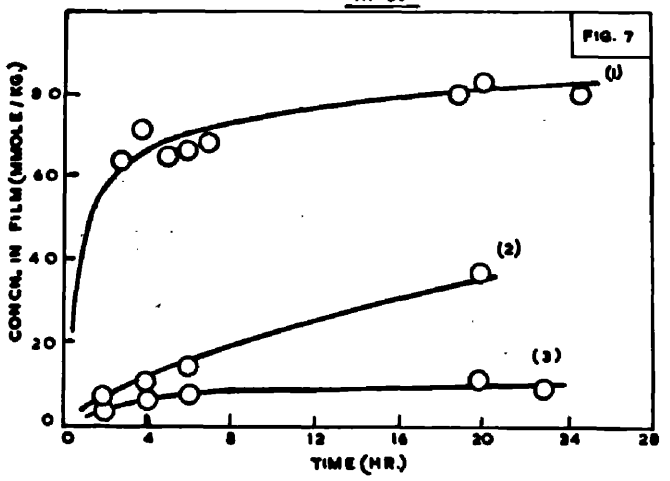
SCALE A: ML. ALUMINIUM SULPHATE SOLN. PER 5 ML. ALIZARIN SOLN.

SCALE B: MOLS. ALIZARIN PER ATOM ALUMINIUM.

ADSORPTION OF SOLWAY BLUE B

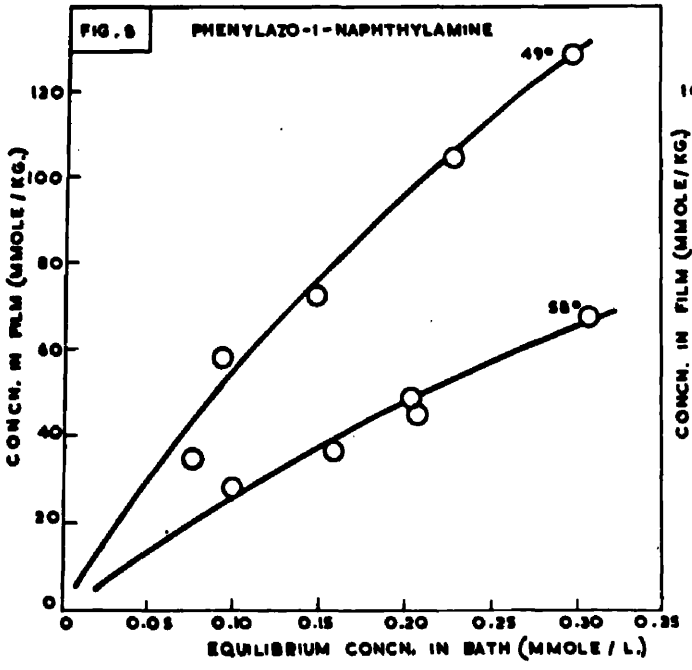


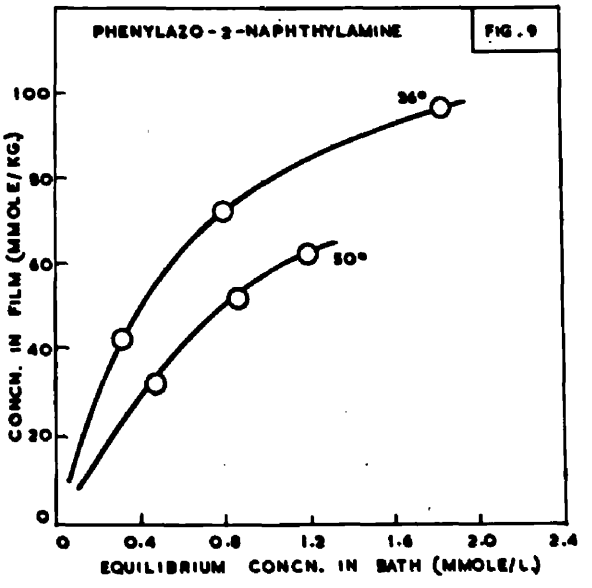
RATE OF ADSORPTION OF MAGENTA P
AT 59°



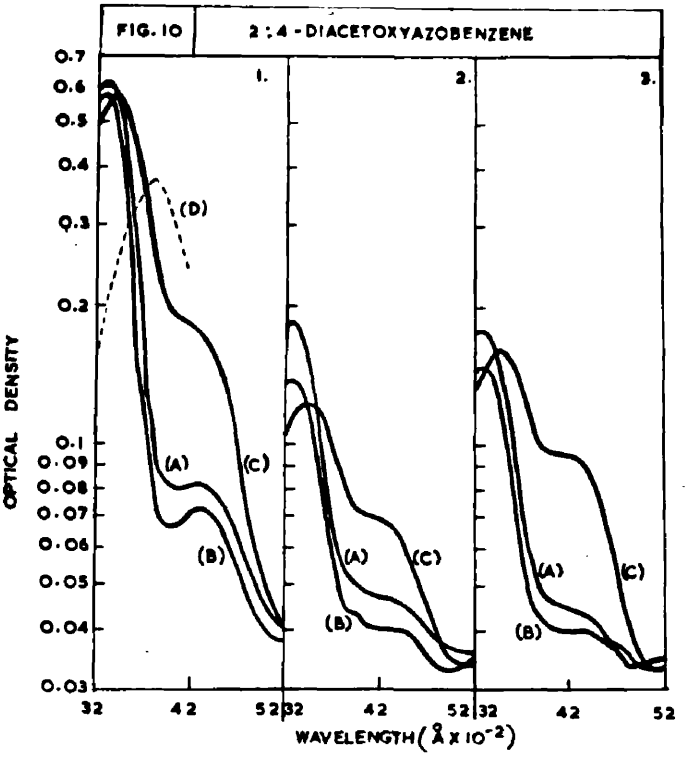
(1) SOLVENT = DIOXAN. (2) SOLVENT = DIOXAN/WATER (75:25).
(3) SOLVENT = DIOXAN/WATER (50:50).

EQUILIBRIUM ADSORPTION ISOTHERMS





LIGHT ABSORPTION CURVES



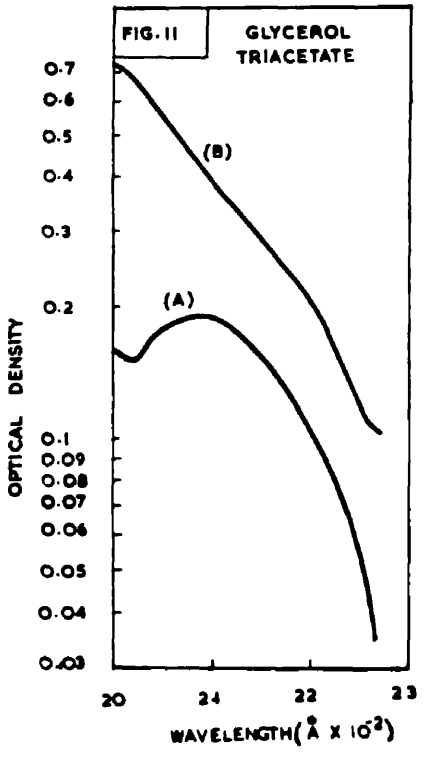
1. 0.2 % SOLN. ; 2. 0.1 % SOLN. ; 3. 0.02% SOLN.

(A) BEFORE CONTACT WITH ANODIC FILM

(B) AFTER CONTACT FOR 48 HRS AT 33°

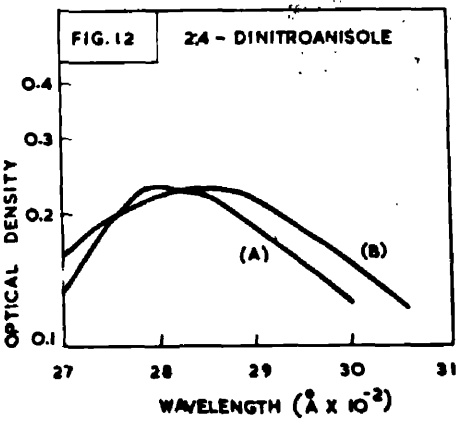
(C) AFTER CONTACT FOR 24 HRS AT 60°

(D) 2:4 - DIHYDROXYAZOBENZENE, 0.2 % SOLN.



(A) 0.015% SOLN. BEFORE CONTACT WITH FILM.

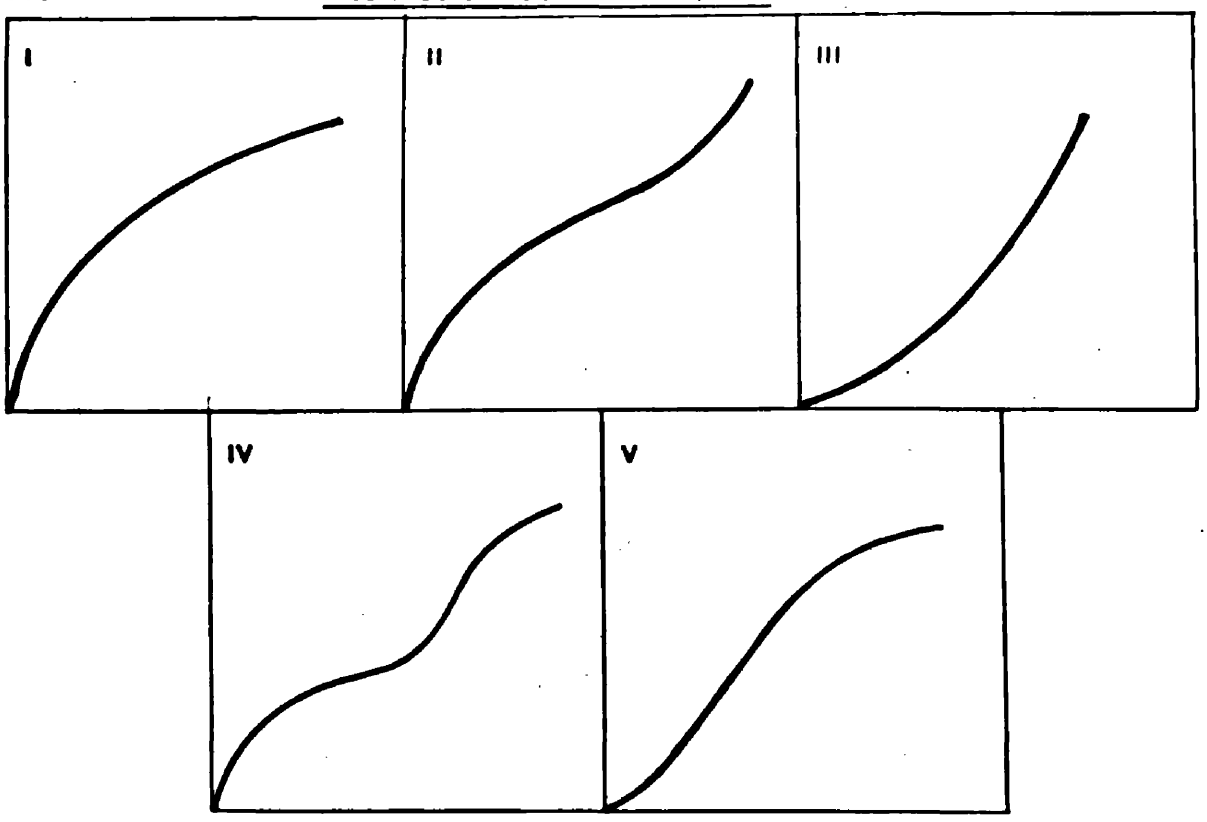
(B) AFTER CONTACT WITH FILM.



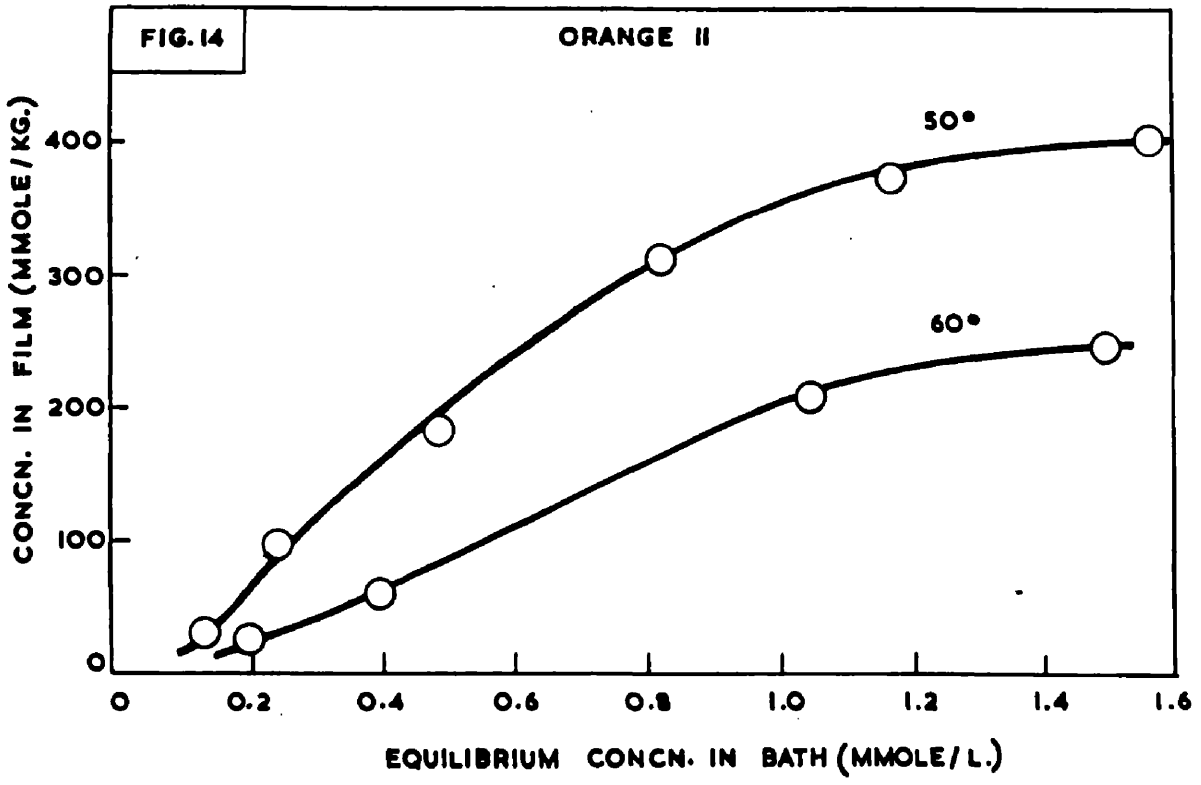
(A) 0.04% SOLN BEFORE CONTACT WITH FILM.

(B) AFTER CONTACT WITH FILM.

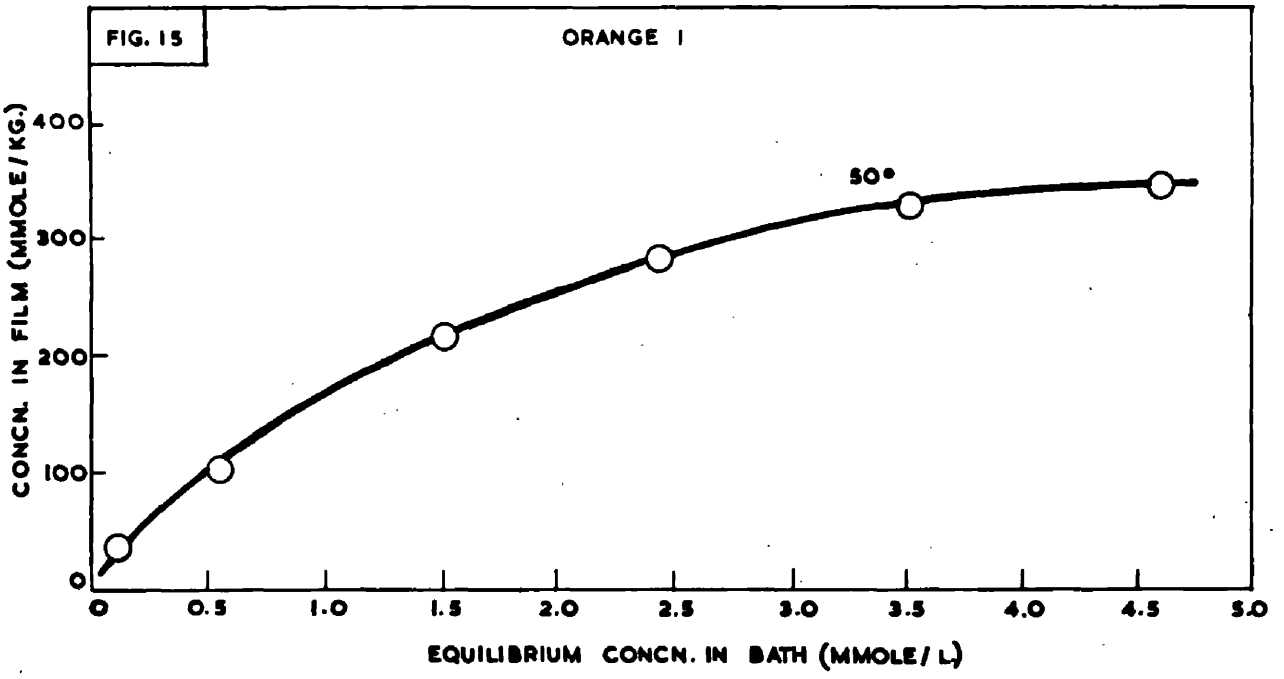
FIG. 13. BRUNAUER ISOTHERM TYPES

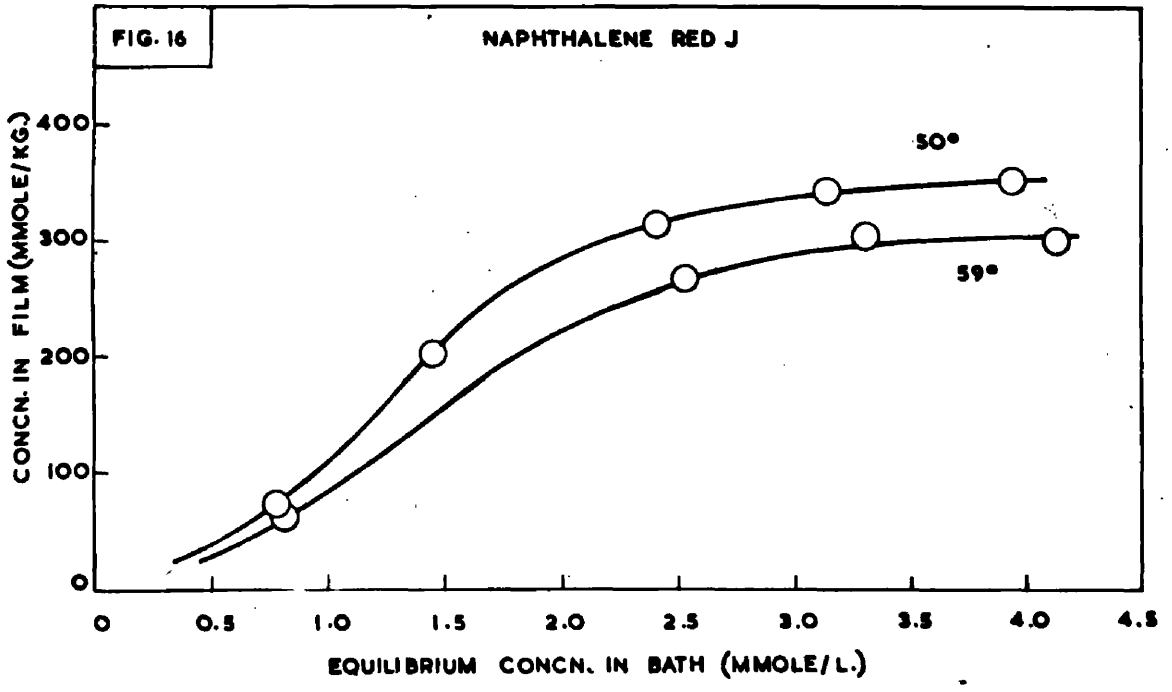


EQUILIBRIUM ADSORPTION ISOTHERMS

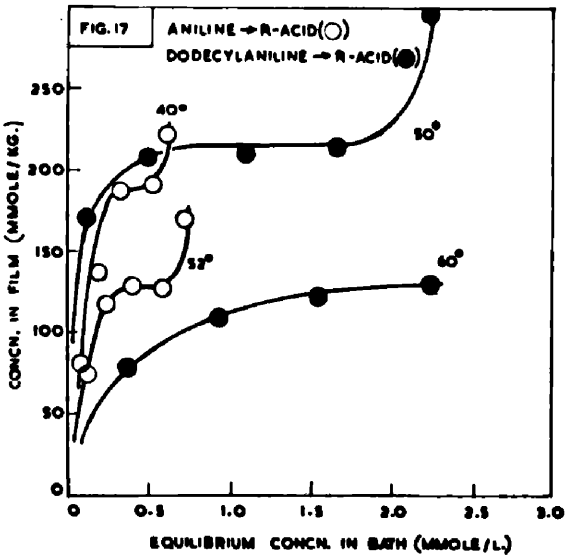


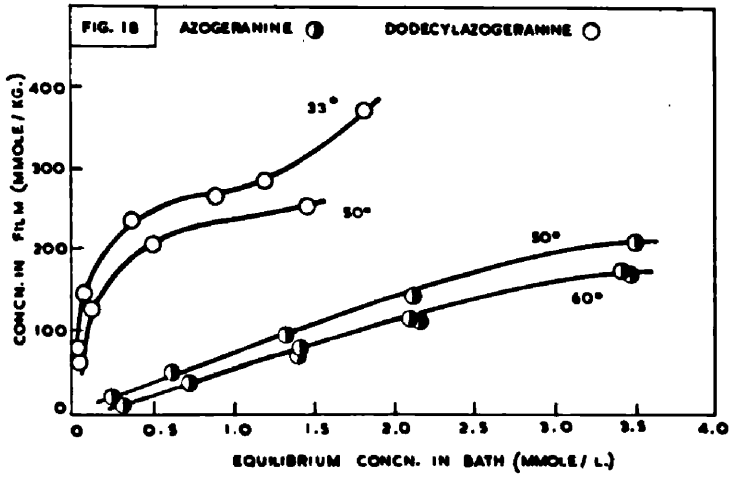
EQUILIBRIUM ADSORPTION ISOTHERMS

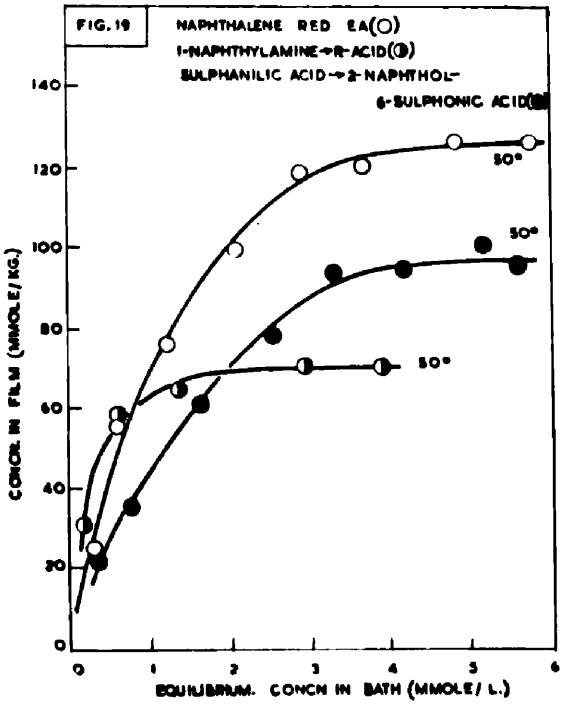




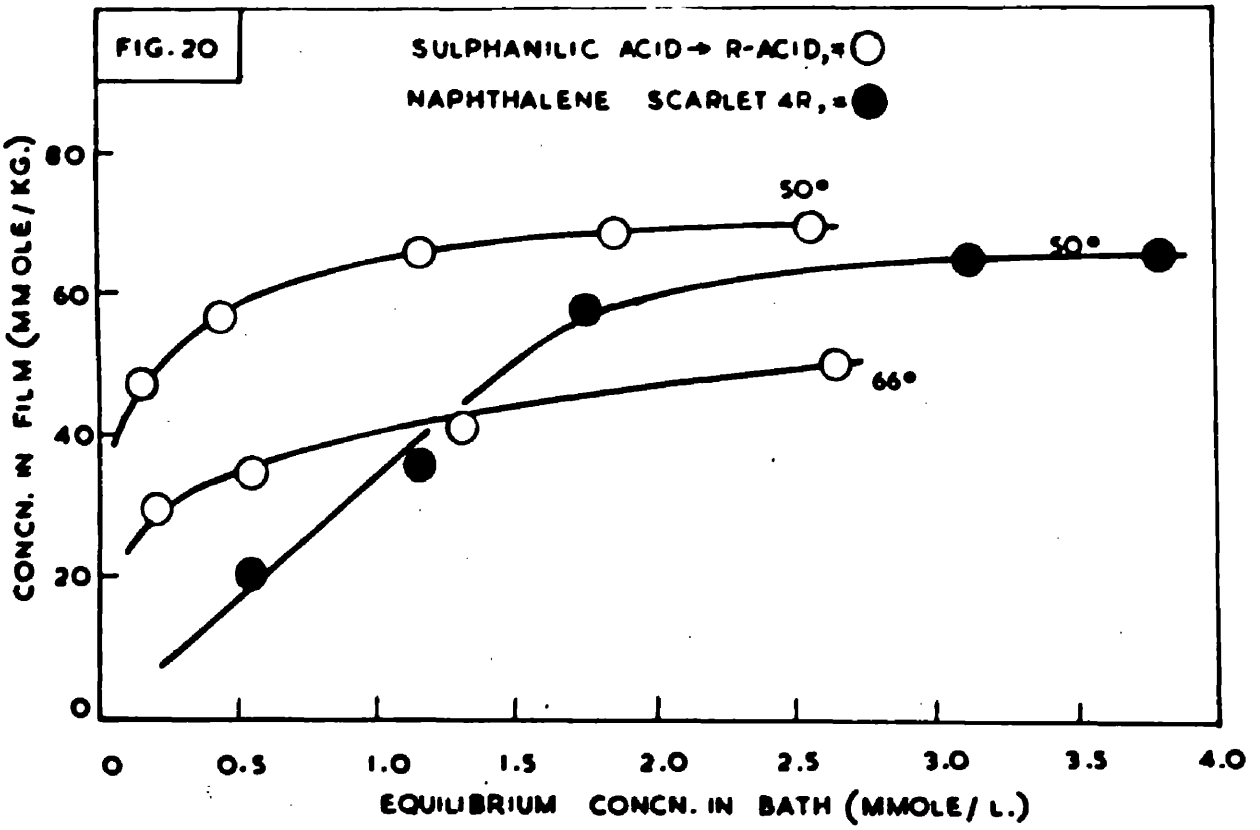
EQUILIBRIUM ADSORPTION ISOTHERMS

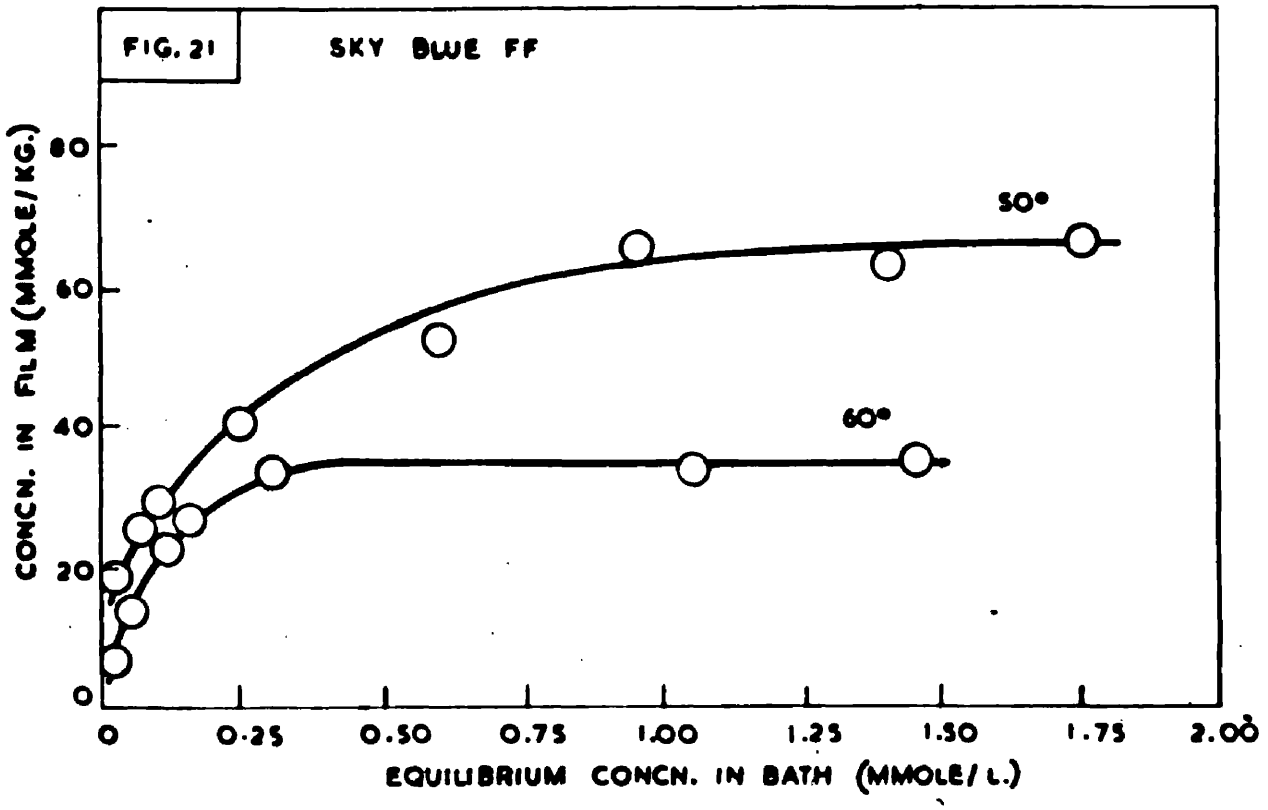






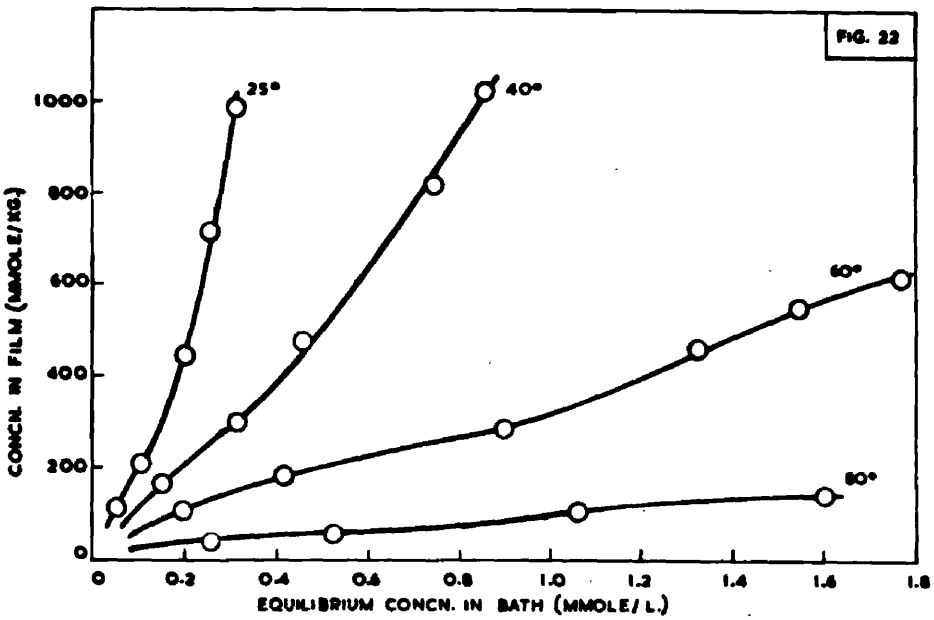
EQUILIBRIUM ADSORPTION ISOTHERMS



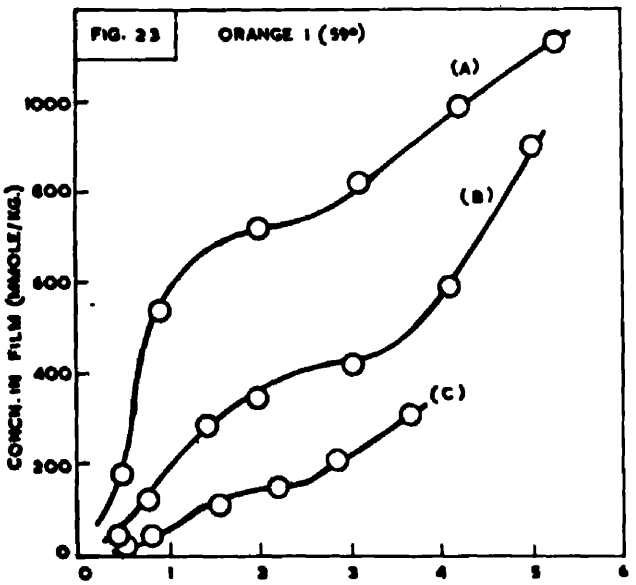


ADSORPTION OF ORANGE I

(H. V. MEHTA)

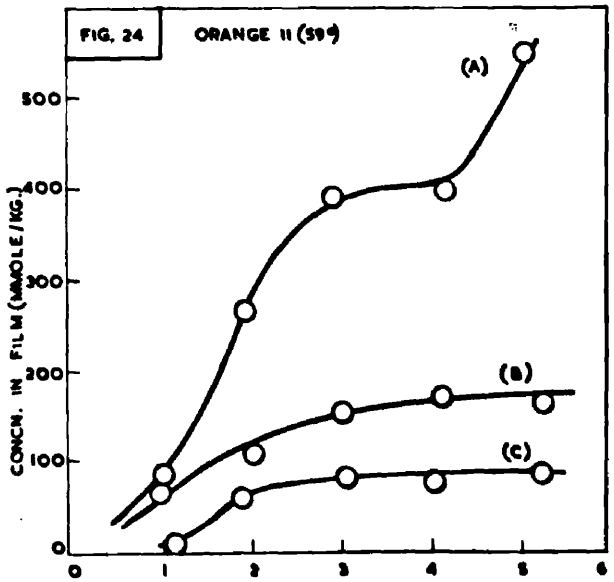


THE EFFECT OF SOLUTION: FILM WEIGHT RATIO ON ADSORPTION



SOLUTION: FILM WGT. RATIOS

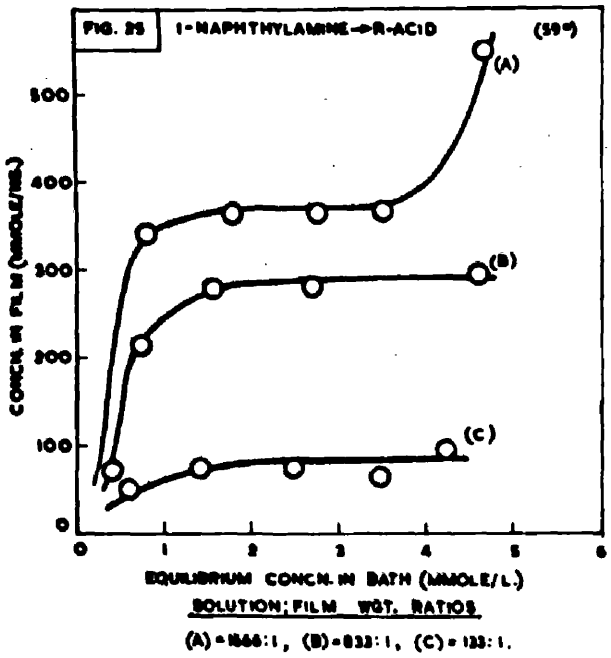
(A)=2500:1, (B)=1250:1, (C)=133:1



SOLUTION: FILM WGT. RATIOS

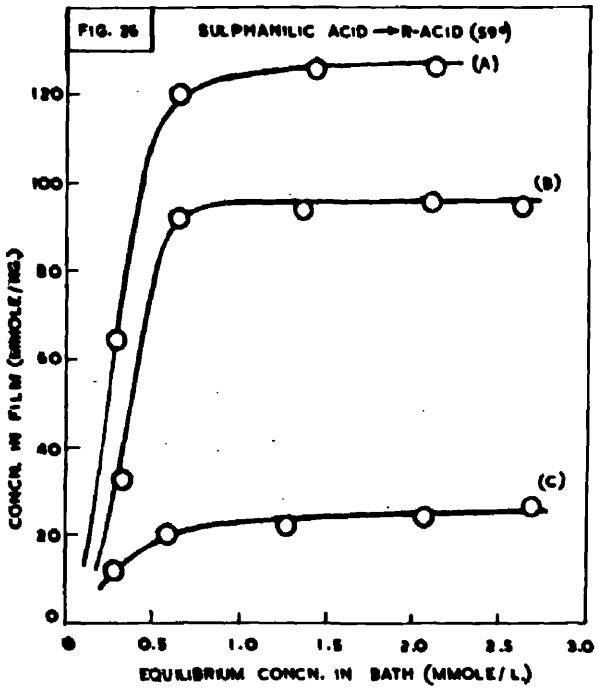
(A)=833:1, (B)=300:1, (C)=133:1.

THE EFFECT OF SOLUTION : FILM WEIGHT RATIO ON ADSORPTION



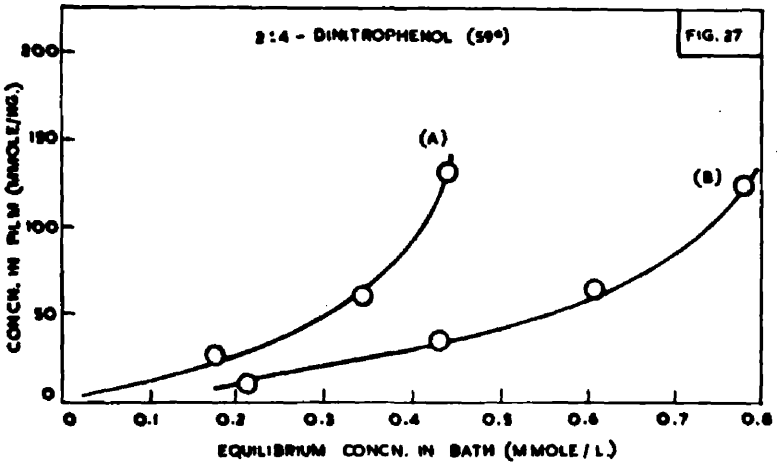
SOLUTION : FILM WGT. RATIOS

(A) = 1666 : 1, (B) = 833 : 1, (C) = 133 : 1.



SOLUTION : FILM WGT. RATIOS

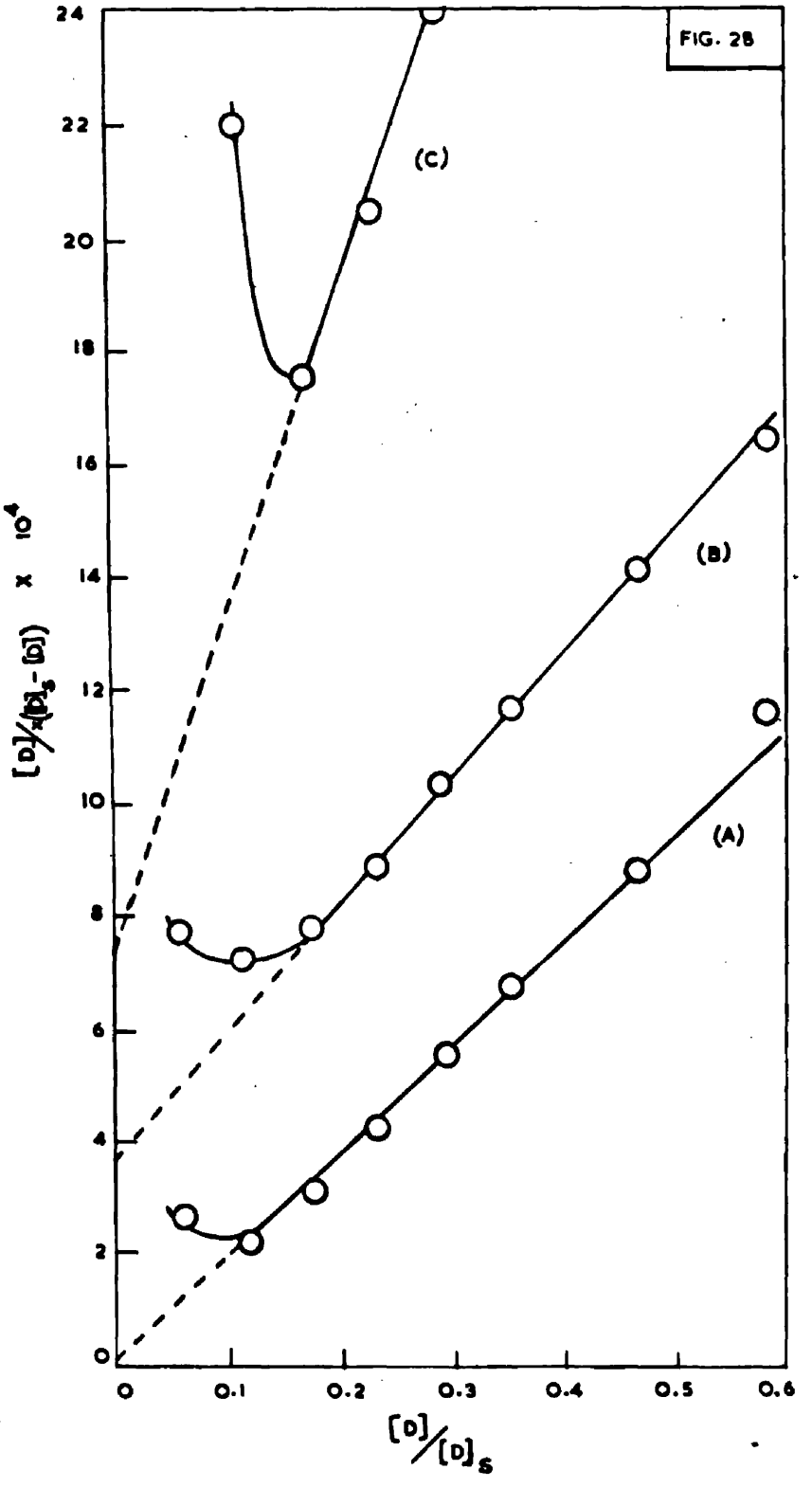
(A) = 1666 : 1, (B) = 833 : 1, (C) = 133 : 1.



SOLUTION : FILM WGT. RATIOS

(A) = 666 : 1, (B) = 200 : 1.

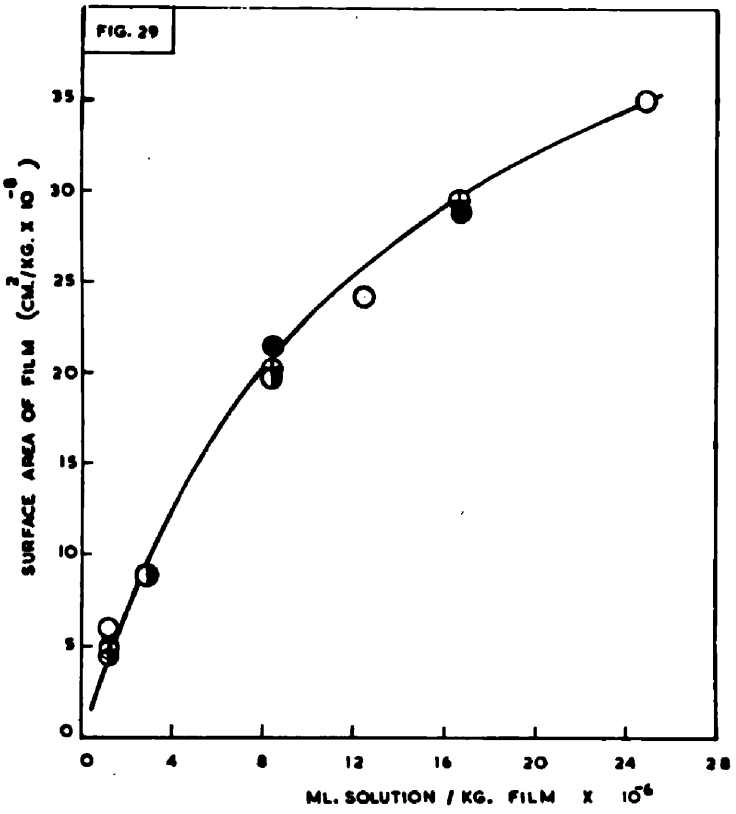
APPLICATION OF B.E.T. EQUATION TO THE ADSORPTION OF ORANGE I



SOLUTION: FILM WGT. RATIOS

(A)=2500:1, (B)=1250:1, (C)=133:1.

VARIATION OF FILM SURFACE AREA WITH SOLUTION:FILM WGT. RATIO



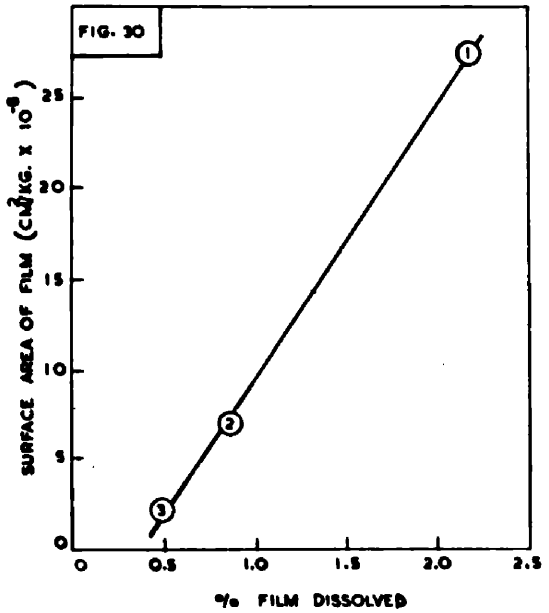
○ = CALCULATED FROM ORANGE I ISOTHERMS (FIG. 23)

◑ = " " ORANGE II " (FIG. 24)

● = " " 1-NAPHTHYLAMINE→R-ACID ISOTHERMS (FIG. 25)

⊕ = " " SULPHANILIC ACID→R-ACID (FIG. 26)

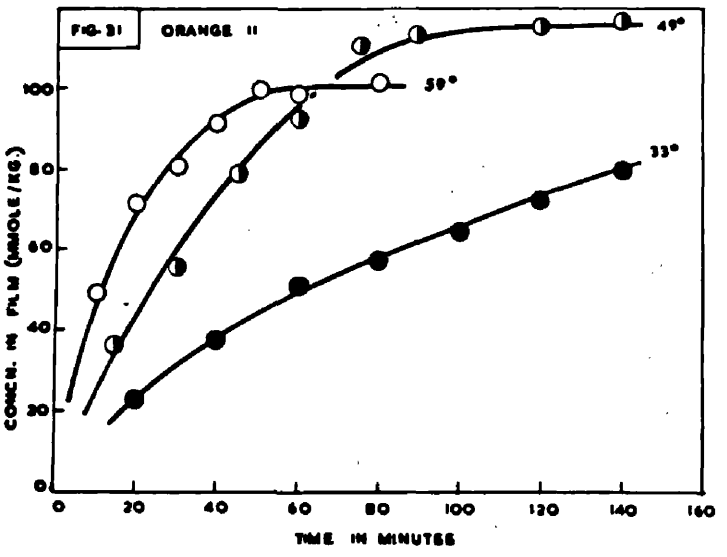
RELATION BETWEEN % FILM DISSOLVED AND SURFACE AREA



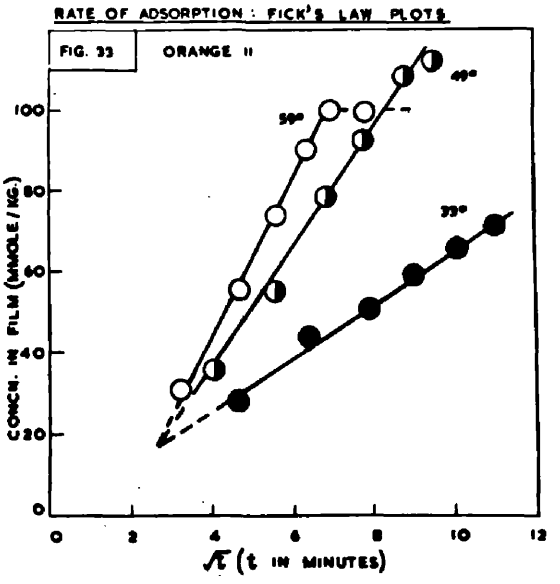
SOLUTION:FILM WGT. RATIOS

① = 1400:1, ② = 300:1, ③ = 150:1.

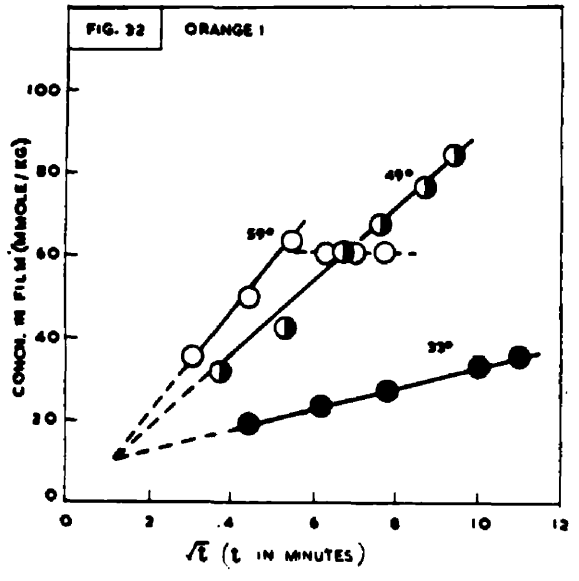
RATE OF ADSORPTION ISOTHERMS

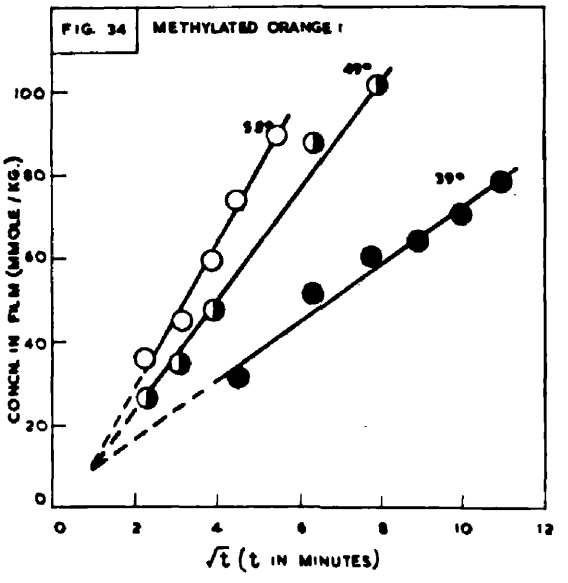


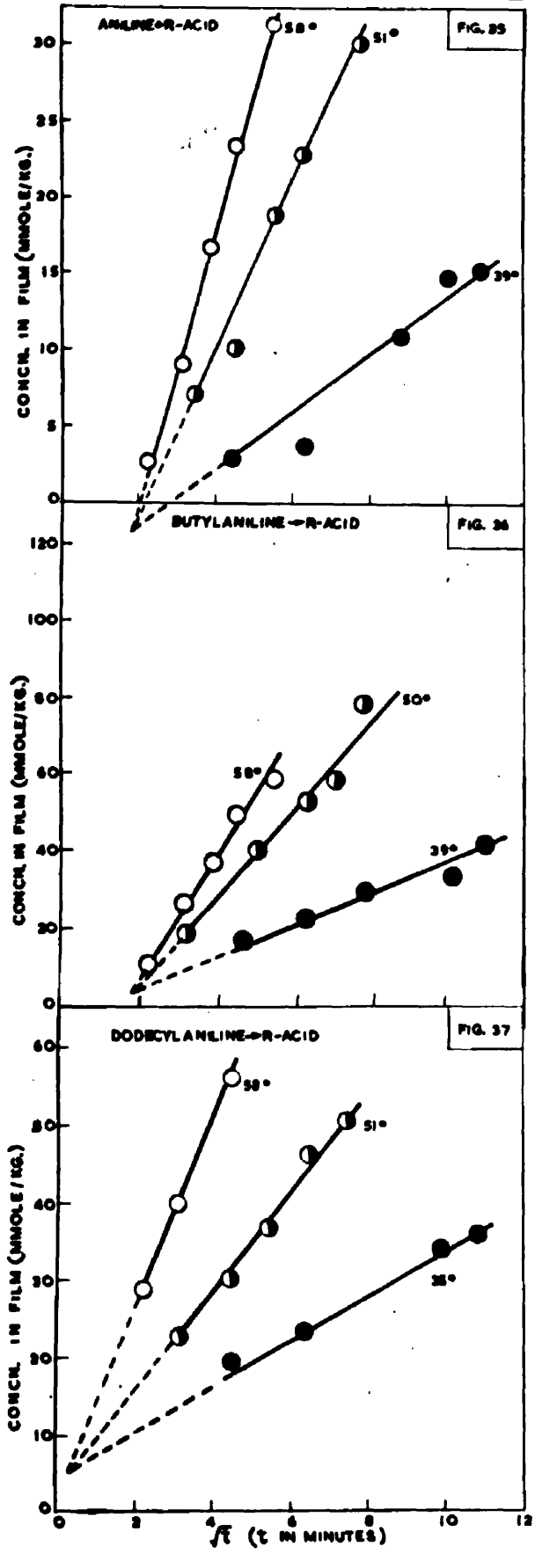
RATE OF ADSORPTION : FICK'S LAW PLOTS

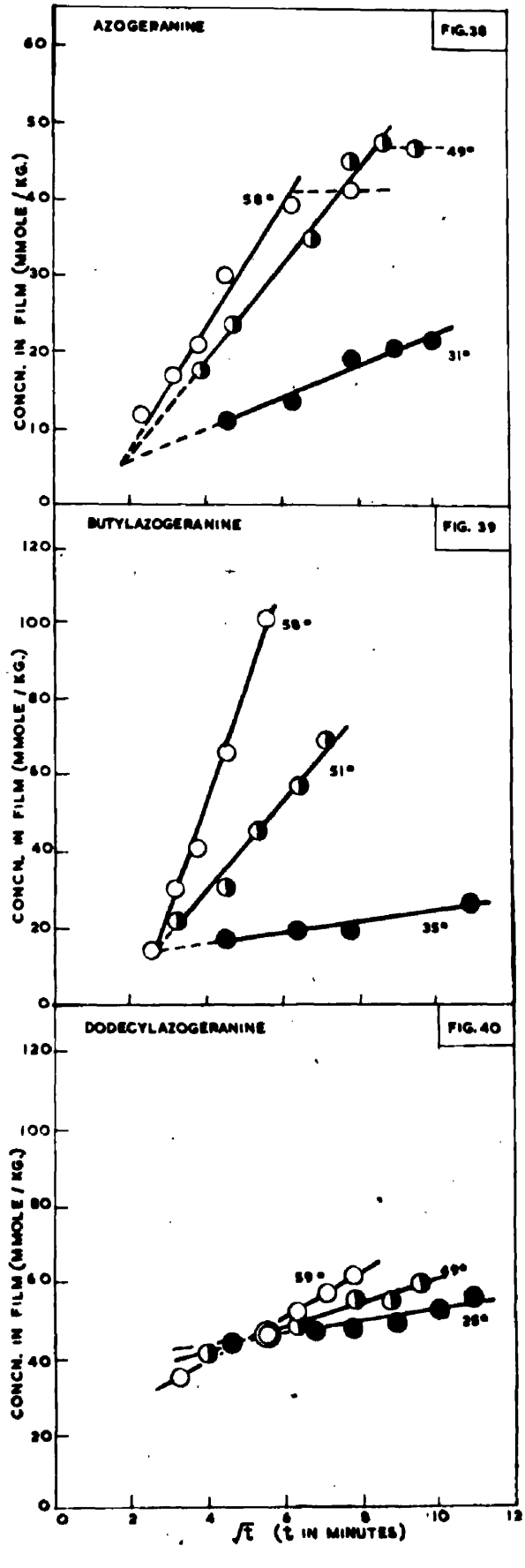


RATE OF ADSORPTION : FICK'S LAW PLOTS

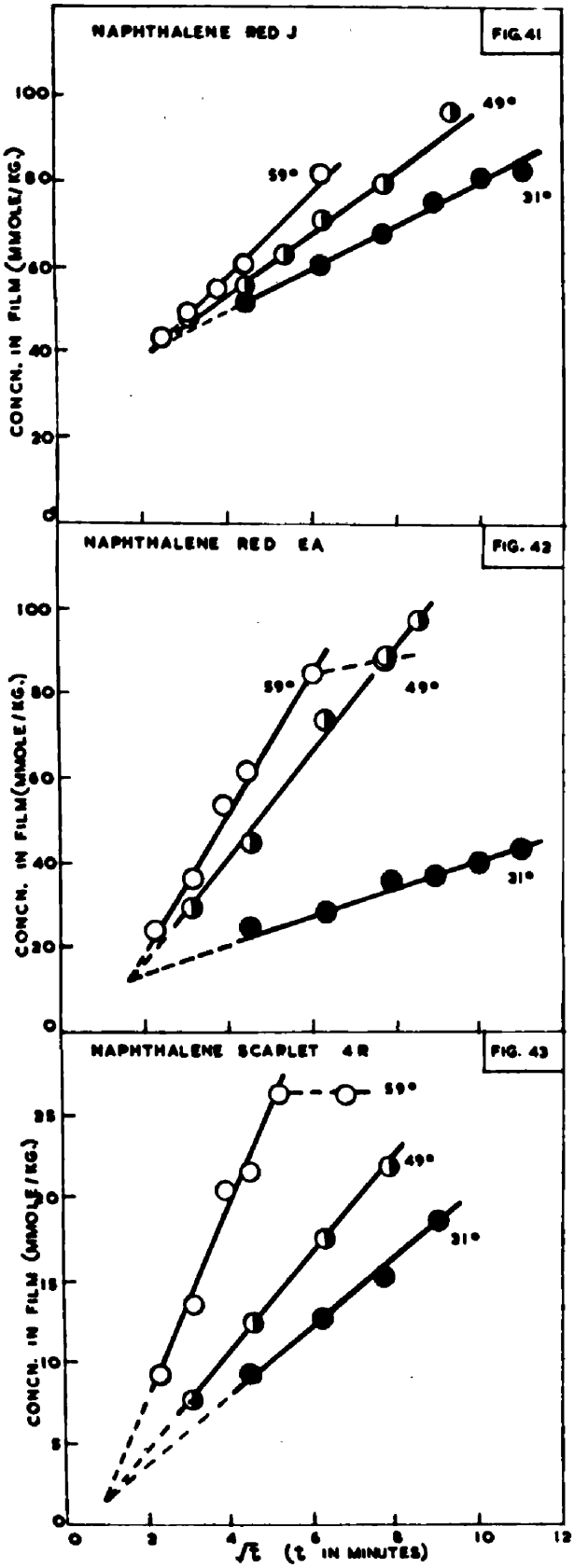


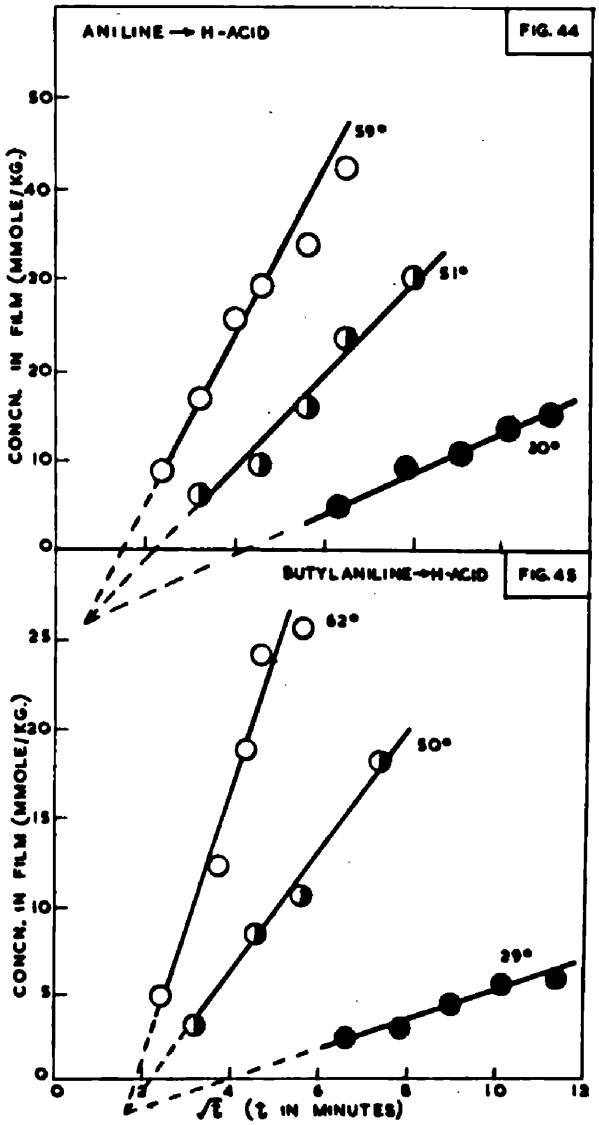



ANILINE→R-ACID
FIG. 35
58°
51°
39°
CONCN. IN FILM (MMOLE/KG.)
BUTYLANILINE→R-ACID
FIG. 36
58°
50°
39°
CONCN. IN FILM (MMOLE/KG.)
DODECYLANILINE→R-ACID
FIG. 37
58°
51°
35°
CONCN. IN FILM (MMOLE/KG.)
√t (t IN MINUTES)

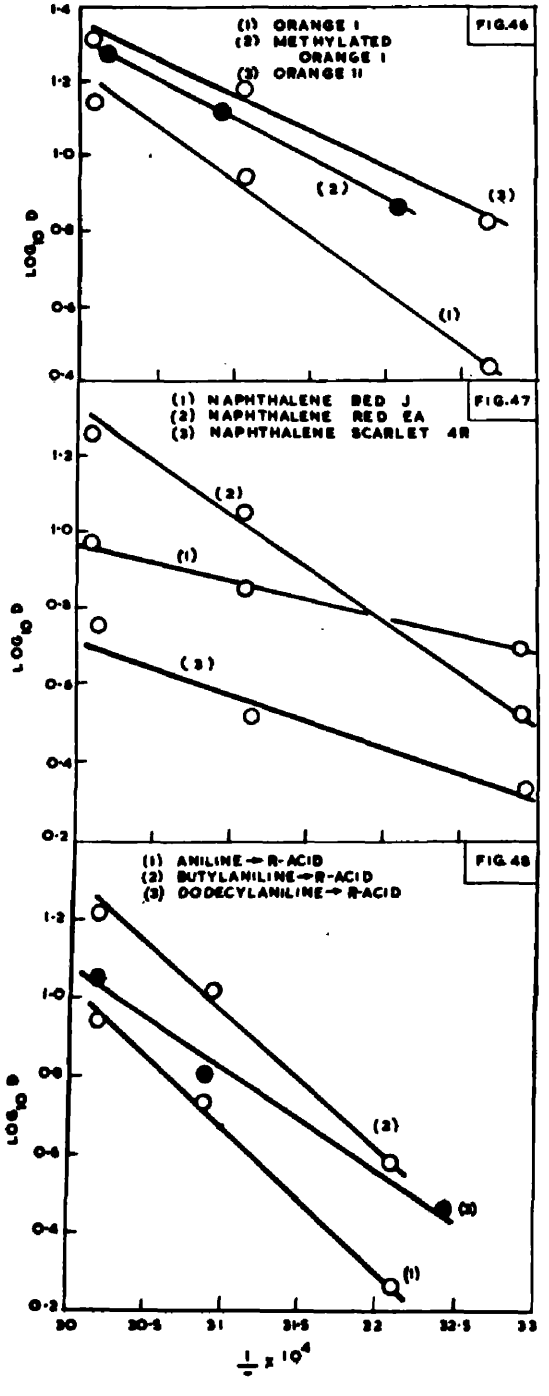

AZOGERANINE
FIG. 38
49°
58°
31°
CONCN. IN FILM (MMOLE/KG.)
BUTYLAZOGERANINE
FIG. 39
58°
51°
35°
CONCN. IN FILM (MMOLE/KG.)
DODECYLAZOGERANINE
FIG. 40
59°
59°
28°
CONCN. IN FILM (MMOLE/KG.)
√t (t IN MINUTES)

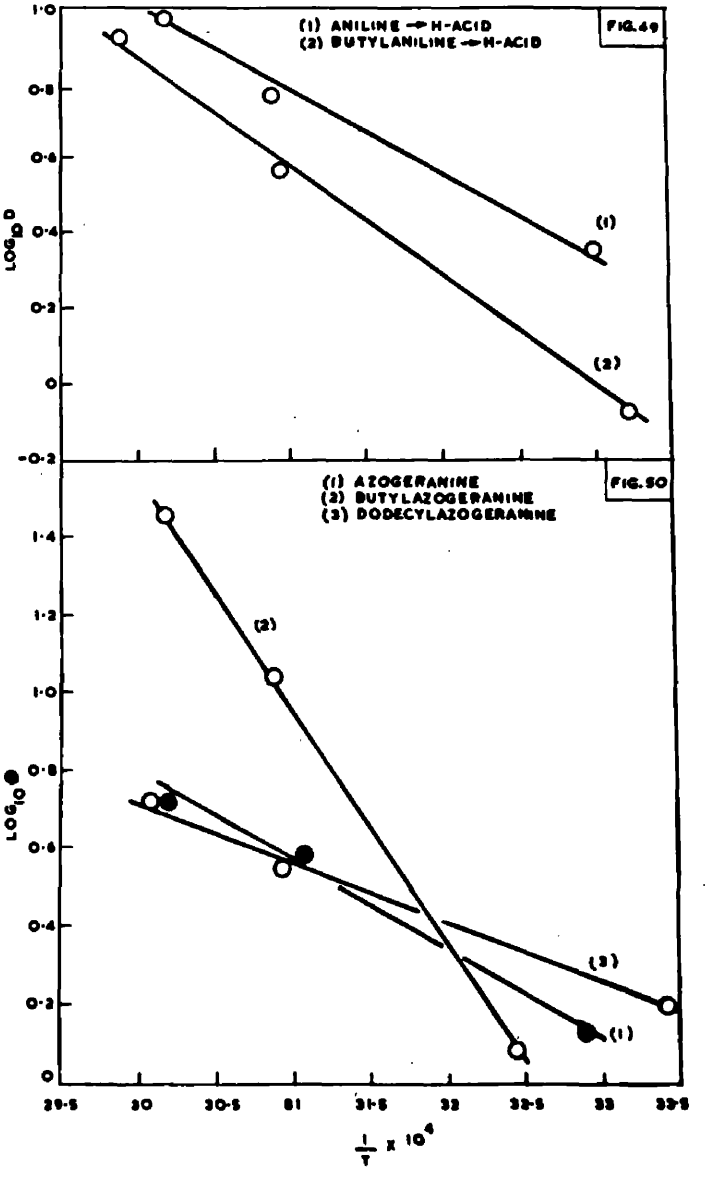
RATES OF ADSORPTION : FICK'S LAW PLOTS



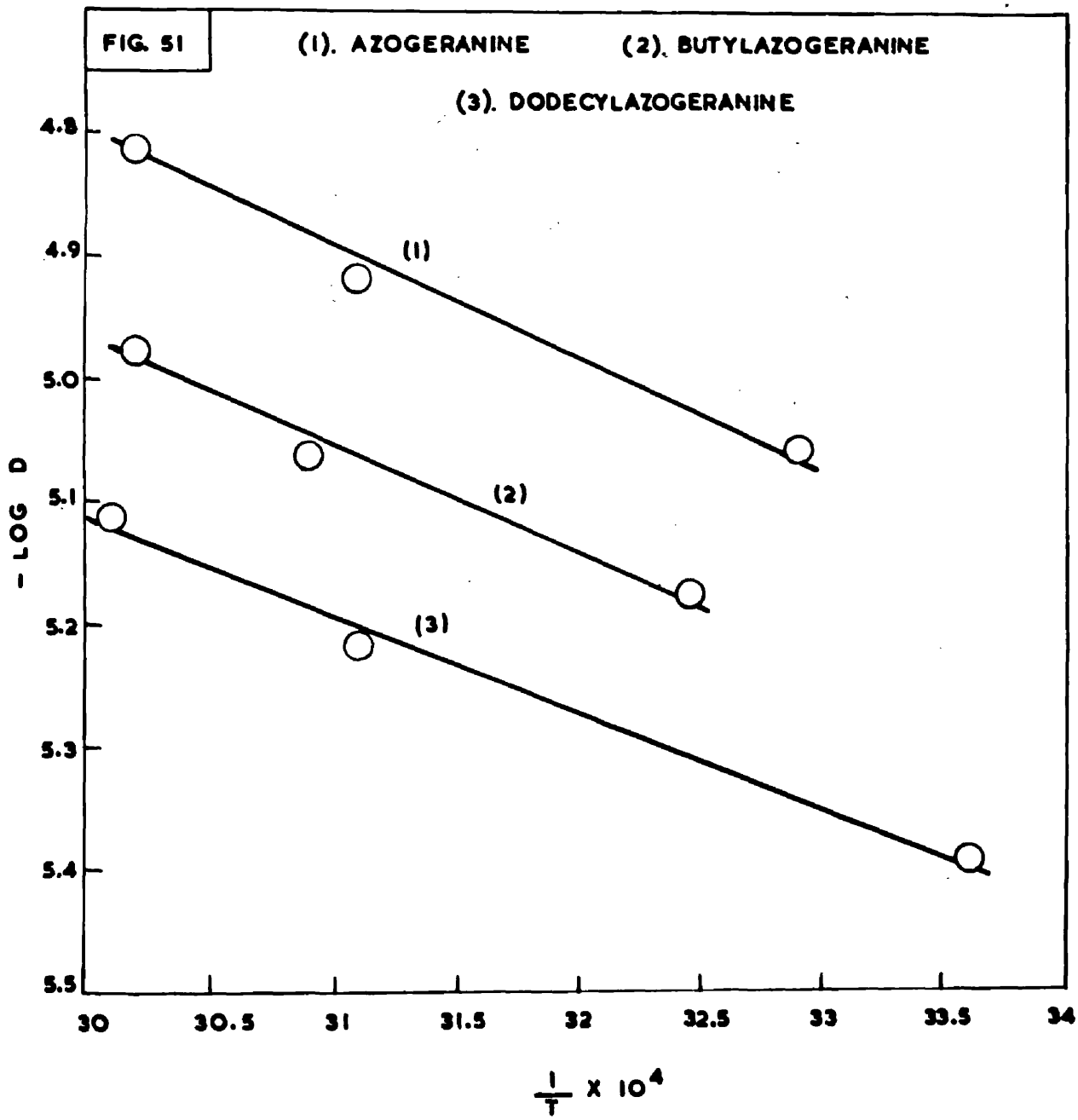


ACTIVATION ENERGY DATA



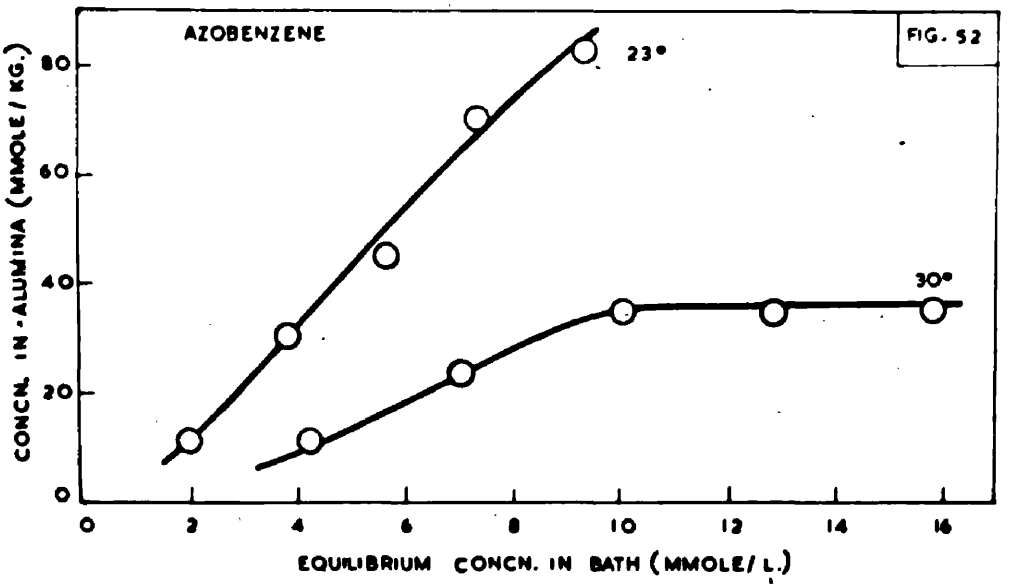


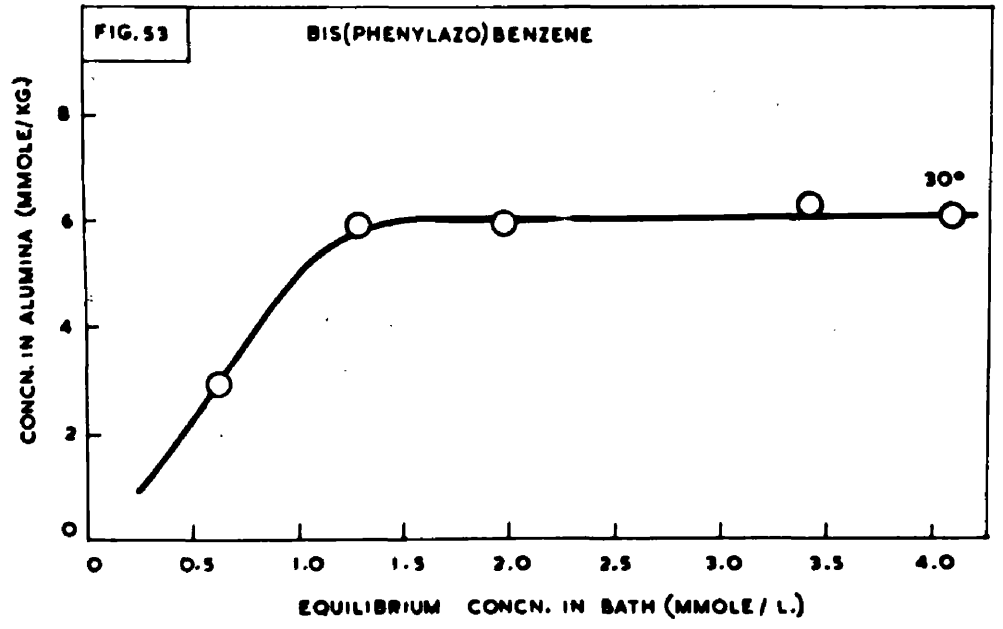
ACTIVATION ENERGY DATA : DIFFUSION IN SOLUTION

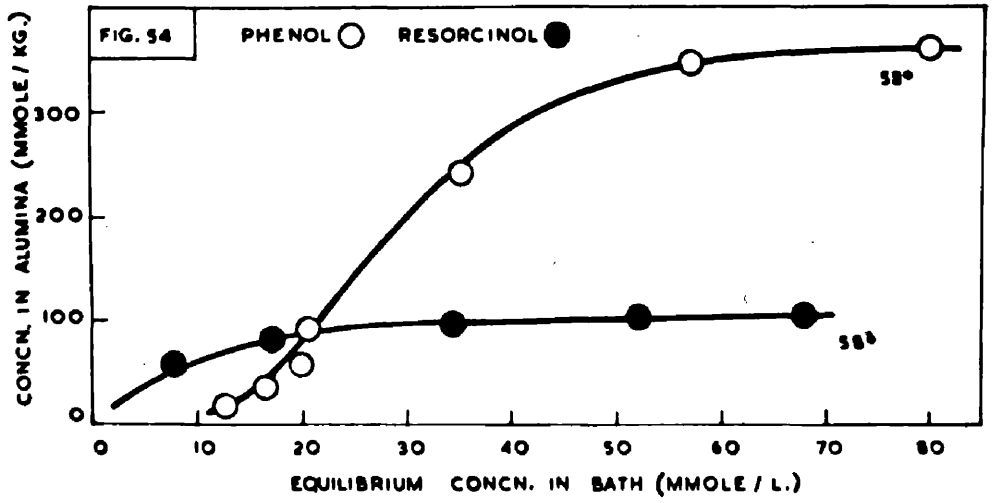


ADSORPTION ON CHROMATOGRAPHIC ALUMINA.

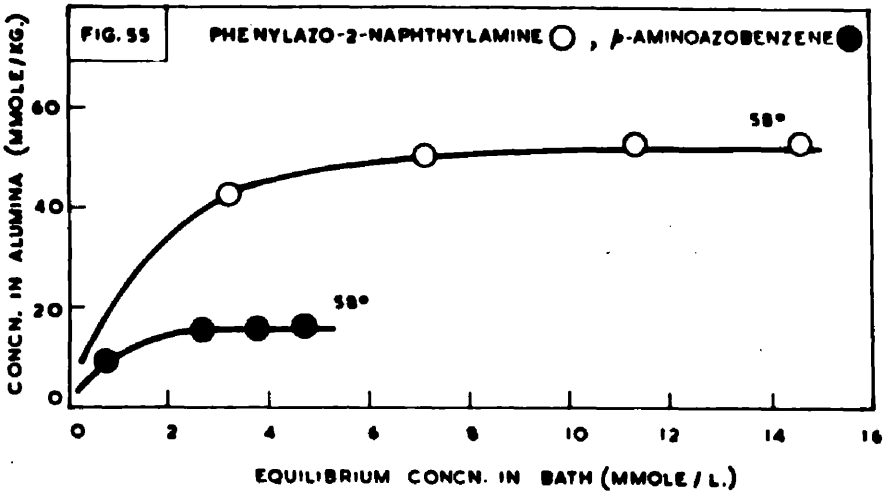
EQUILIBRIUM ADSORPTION ISOTHERMS

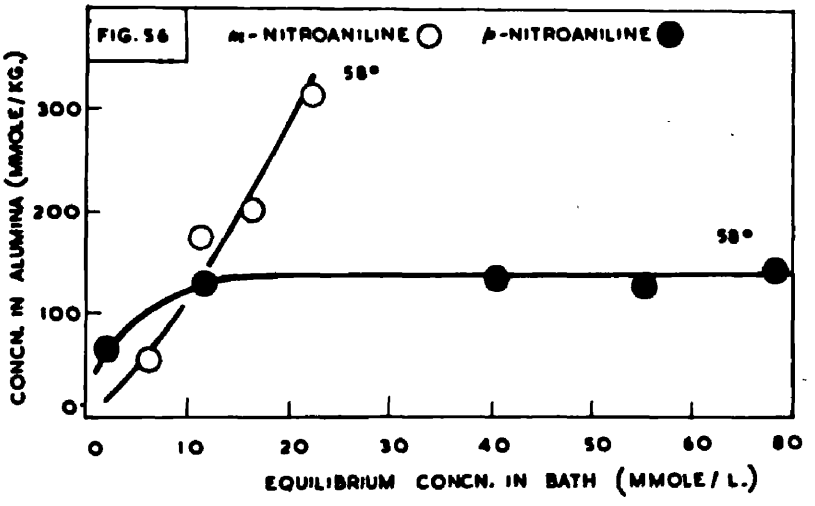


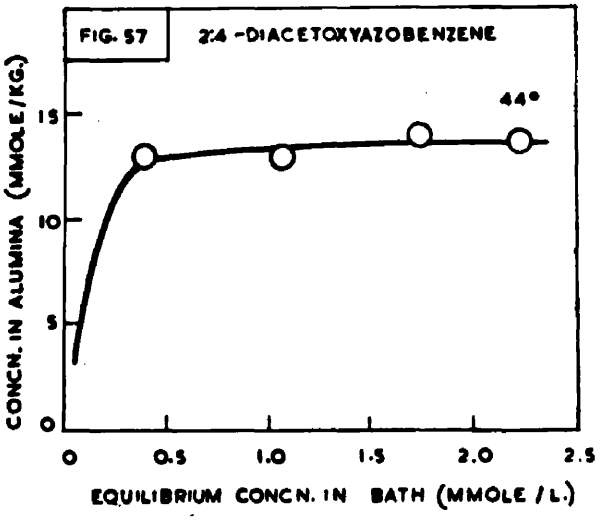


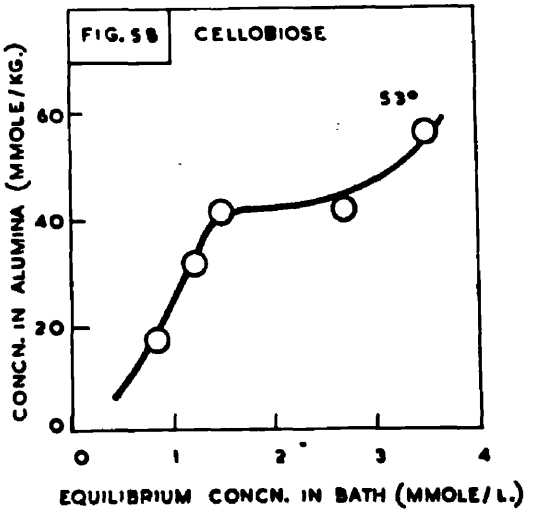


EQUILIBRIUM ADSORPTION ISOTHERMS

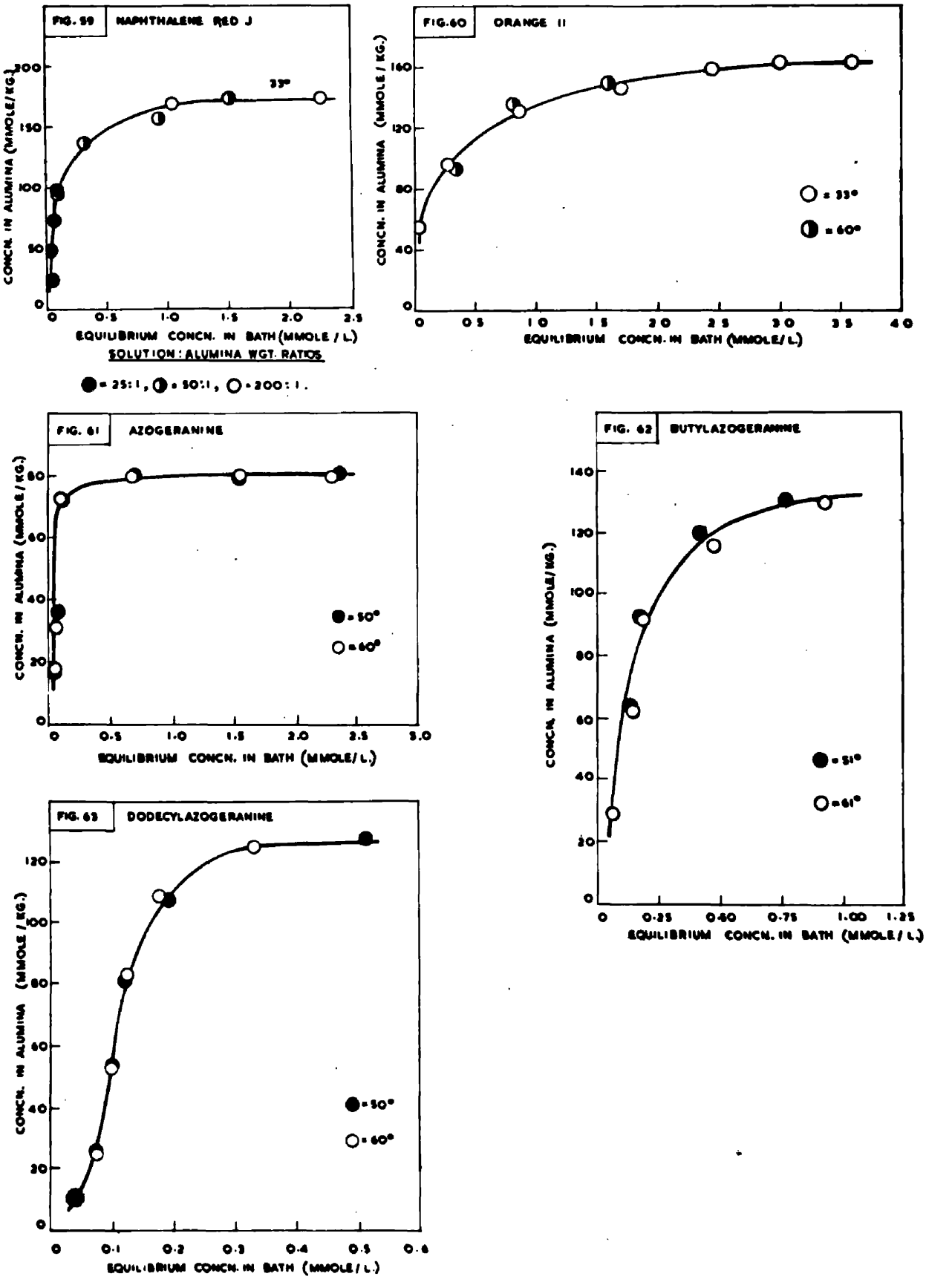




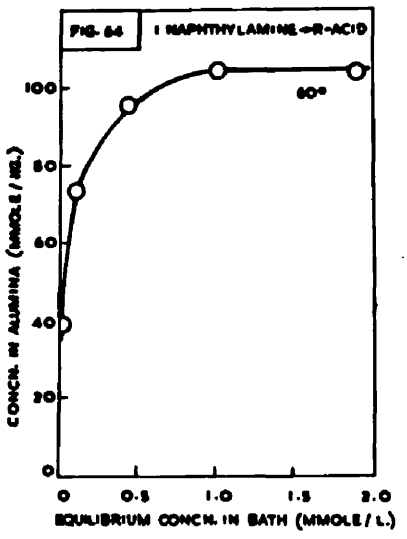


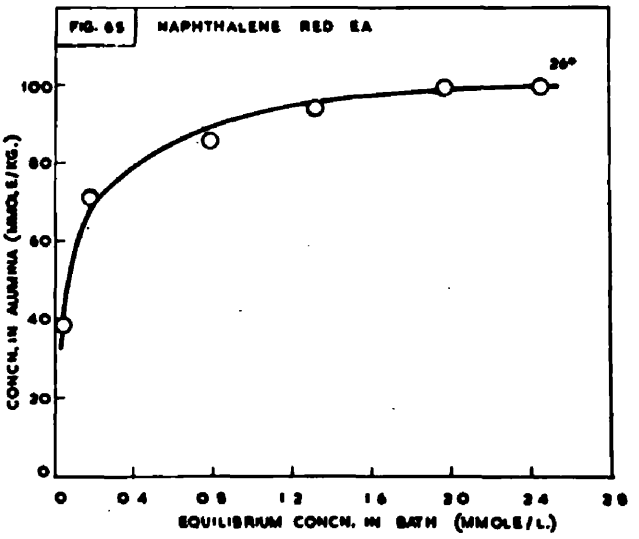


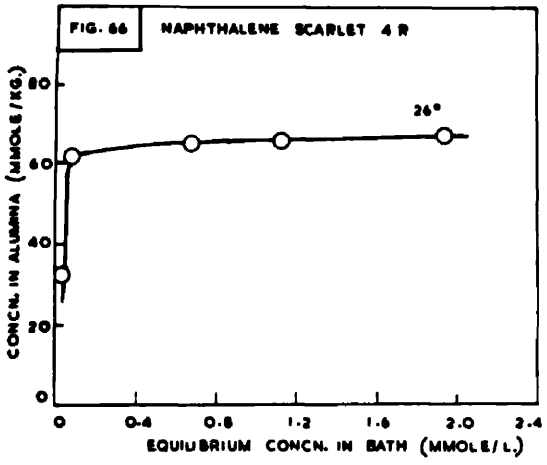
EQUILIBRIUM ADSORPTION ISOTHERMS

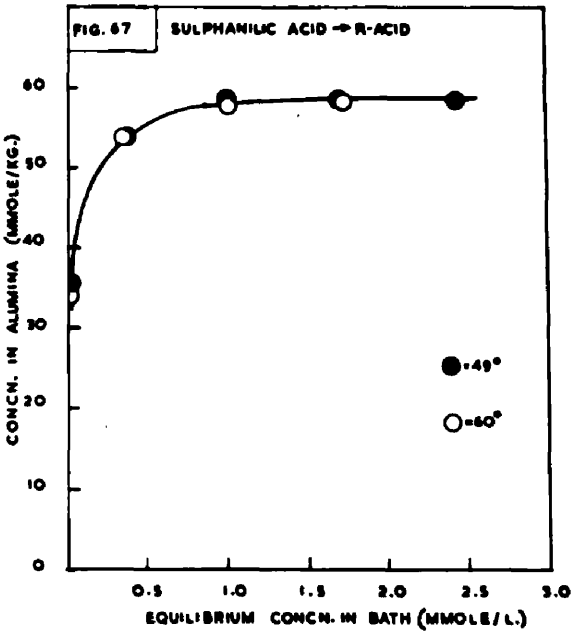


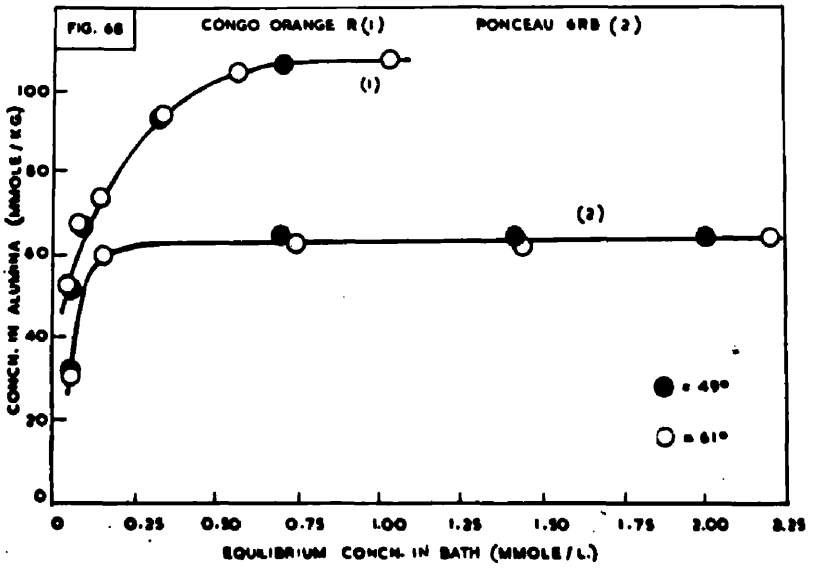
EQUILIBRIUM ADSORPTION ISOTHERMS



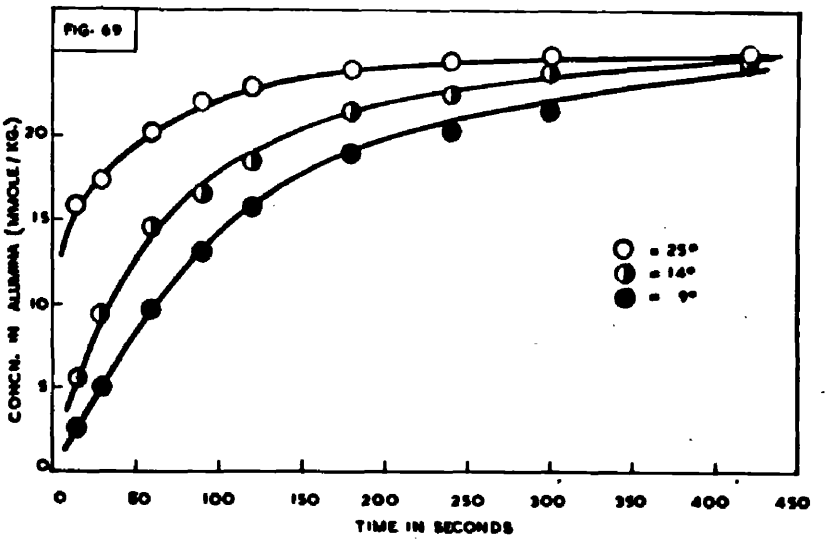




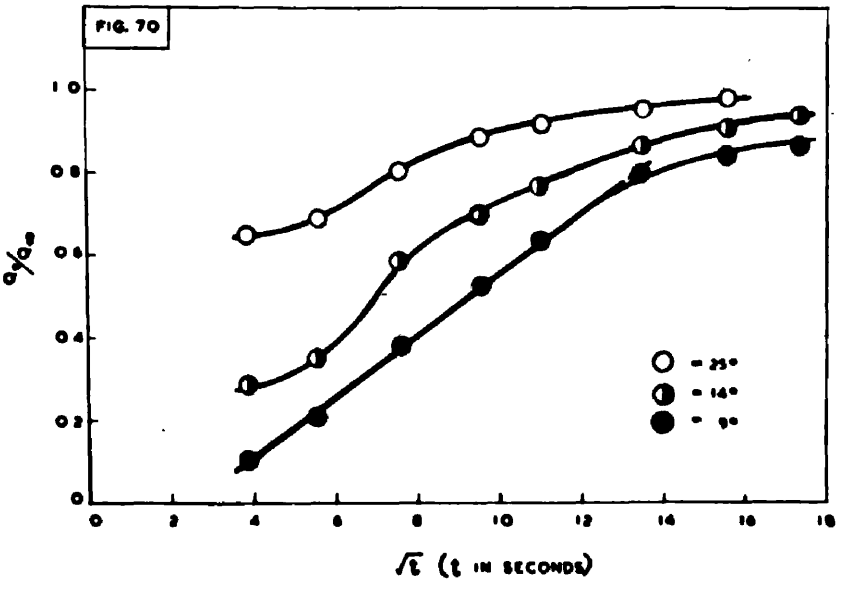




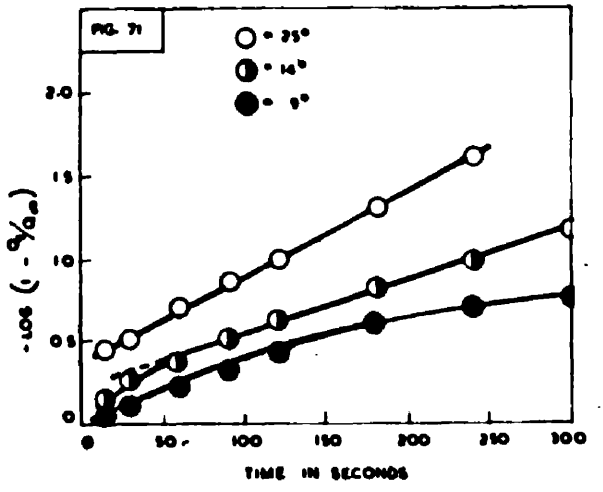
RATE OF ADSORPTION OF NAPHTHALENE RED J



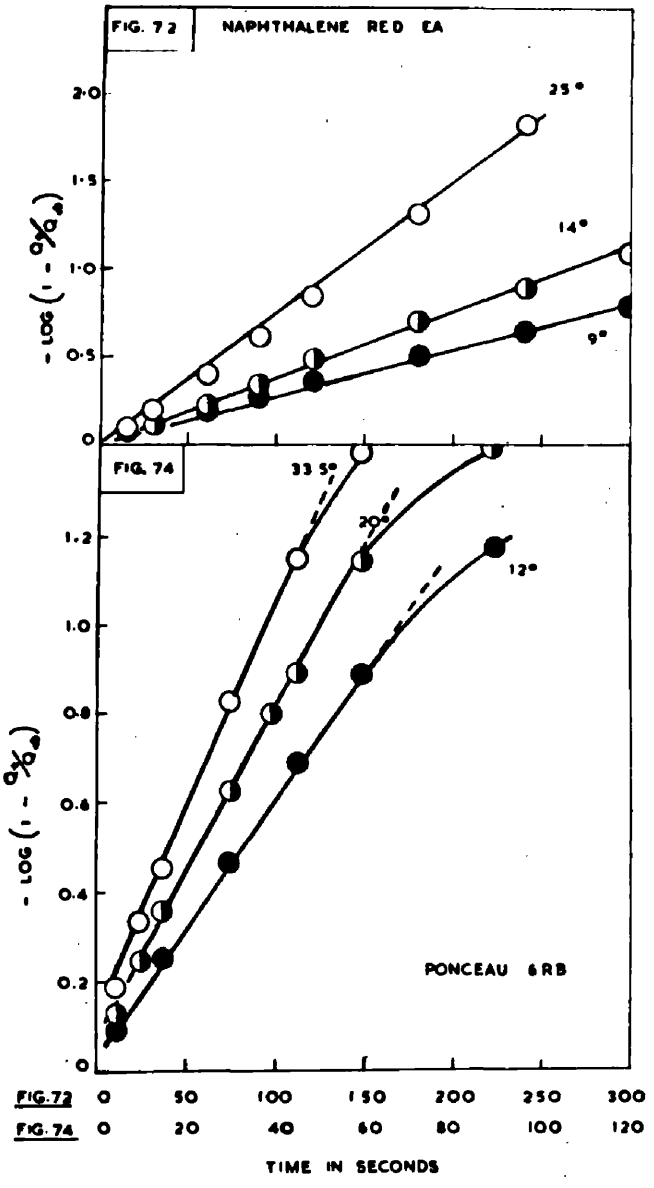
RATE OF ADSORPTION OF NAPHTHALENE RED J : FICK'S LAW BASIS

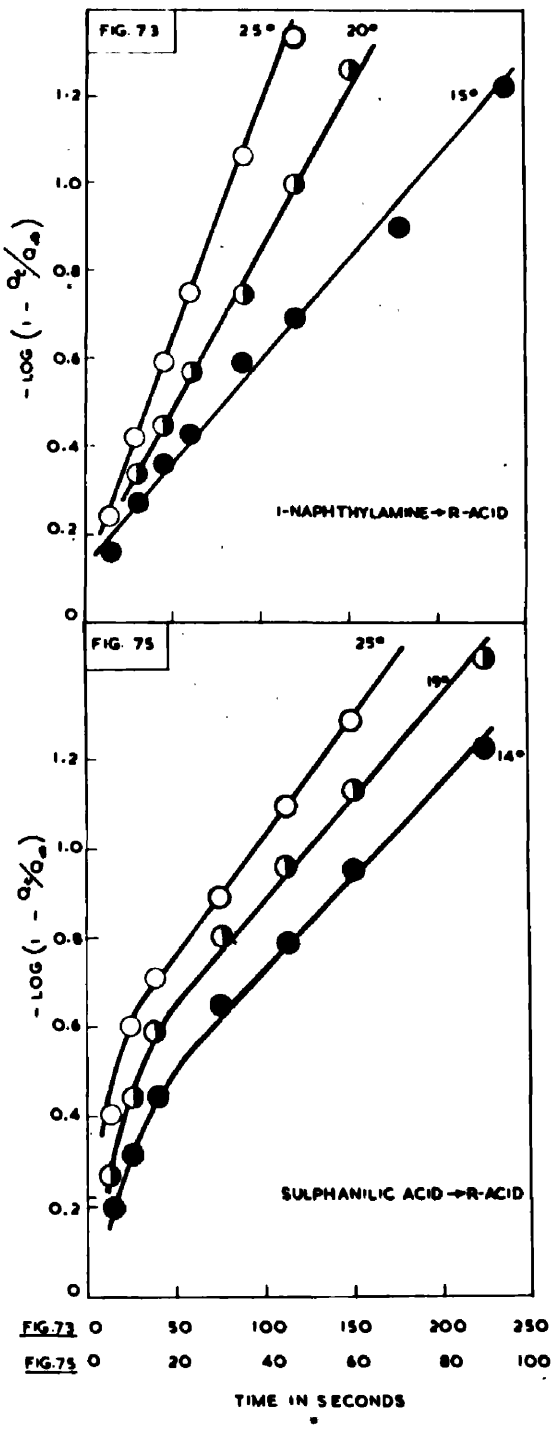


RATE OF ADSORPTION OF NAPHTHALENE RED J FILM DIFFUSION BASIS

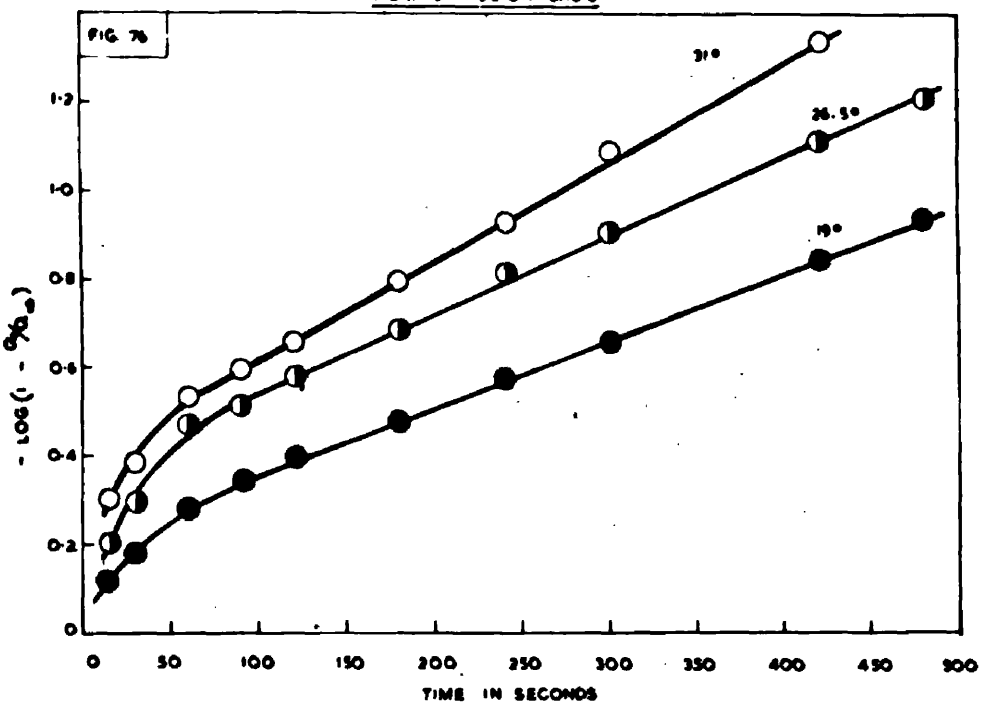


RATE OF ADSORPTION : FILM DIFFUSION BASIS

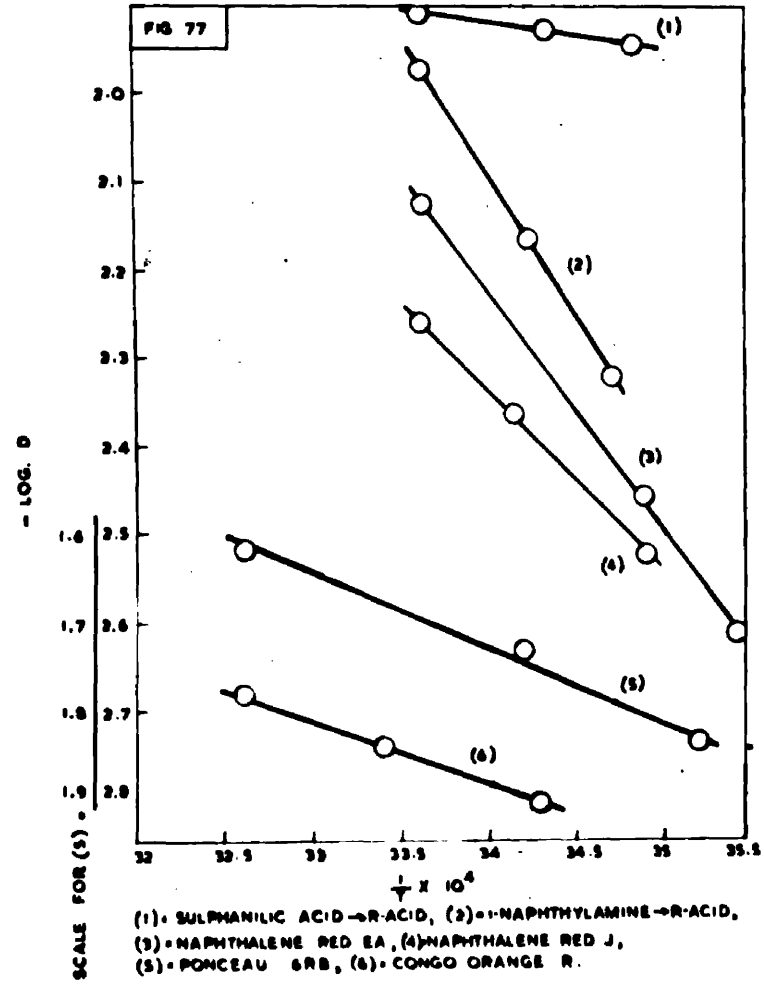




RATE OF ADSORPTION OF CONGO ORANGE R
FILM DIFFUSION BASIS



ACTIVATION ENERGY DATA



(1)• SULPHANILIC ACID→R-ACID, (2)•1-NAPHTHYLAMINE→R-ACID,
(3)•NAPHTHALENE RED BA, (4)NAPHTHALENE RED J,
(5)•PONCEAU 6RB, (6)•CONGO ORANGE R.